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Metal Residue Deposition from Military Pyrotechnic Devices and Field Sampling Guidance

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COVER: Detonation of a M127A1 White Signal Parachute Flare at Camp Ethan Allen, VT.

May 2012

Metal Residue Deposition from Military Pyrotechnic Devices and Field Sampling Methods

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Filtered snow, solid residue from snow filtering, tray deposit, cartridge rinseate, and soil samples were collected. Metals were detected in the snow samples but the concentrations were very low. Similarly, soil sample results indicated the metal loading could not be distinguished from background. Metals deposition was greatest for those devices detonated on the ground surface. Apparently, dispersion in air circulates the particulate residue over such a large area that significant metal accumulation does not occur. Loadings sufficient to exceed metal regulatory levels would require hundreds of detonations in the same area with little air dispersion.

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Nomenclature

BRAC	base realignment and closure
CCV	continuing calibration verification
COPC	contaminant of potential concern
CRREL	Cold Regions Research and Engineering Laboratory
DOD	Department of Defense
DU	decision unit
EDAX	energy dispersive X-ray analysis
EL	Environmental Laboratory
ERDC	Engineering Research and Development Center
FUDS	formerly used defense sites
FY	fiscal year
HC	Hexachloroethane
ICP-MS	inductively coupled plasma - mass spectrometry
ICP-OES	inductively coupled plasma – optical emission spectrometry
K_ds	soil partitioning coefficient
LCS	laboratory control sample
MIDAS	Munitions Items Disposition Action System
MMR	Massachusetts Military Reservation

MMRP	Military Munition Response Program
PRG	preliminary remediation goal
QA	quality assurance
RI	remedial investigation
RPD	relative percent difference
RSD	relative standard deviation
SEM	scanning electron microscope
SI	site investigation
USEPA	US Environmental Protection Agency
UXO	unexploded ordnance
WWI	World War I
WWII	World War II
XRD	X-ray diffraction

Preface

This report was prepared by Jay L. Clausen, Biogeochemical Sciences Branch (BSB), U.S. Army Engineer Research and Development Center (ERDC), Cold Regions Research and Engineering Laboratory (CRREL), Hanover, New Hampshire.

The U. S. Army Environmental Command (AEC) provided funding for this work. The support of Camp Ethan Allen, VT and Bruce Beauregard was instrumental in performing the tests discussed in this report. Louise Parker and Marianne Walsh, CRREL, provided technical reviews.

This report was prepared under the general supervision of Terrence Sobecki, Branch Chief, BSB, CRREL; Dr. Lance D. Hansen, Deputy Director, CRREL; and Dr. Robert E. Davis Director, CRREL. The Commander and Executive Director of the ERDC is Colonel Gary E. Johnston. The Director is Dr. Jeff Holland.

Unit Conversion Factors

Multiply	By	To Obtain
acres	4,046.873	square meters
cubic feet	0.02831685	cubic meters
cubic inches	1.6387064 E-05	cubic meters
cubic yards	0.7645549	cubic meters
degrees Fahrenheit	(F-32)/1.8	degrees Celsius
feet	0.3048	meters
hectares	1.0 E+04	square meters
inches	0.0254	meters
microns	1.0 E-06	meters
miles (U.S. statute)	1,609.347	meters
pounds (mass)	0.45359237	kilograms
square feet	0.09290304	square meters

1 Introduction

The US Army's Military Munitions Response Program (MMRP) was established under the Defense Environmental Restoration Program in 2001 to manage the environmental, health, and safety issues associated with unexploded ordnance (UXO), discarded military munitions, and munitions constituents on non-operational ranges located on active installations, on Defense Base Realignment and Closure (BRAC) sites and Formerly Used Defense Sites (FUDS). Under the MMRP, the Department of Defense (DoD) is required to: 1) inventory non-operational ranges containing or are suspected to contain munitions-related material released before September 2002; 2) identify, characterize, track, and report data on MMRP sites and clean-up activities; and 3) develop a process to prioritize site cleanup and estimate costs. The Army completed their inventory of non-operational ranges in 2003 and began Site Investigations (SIs) of these MMRP sites. Based on the SI findings some ranges require additional assessment under the Remedial Investigation (RI) process.

Pyrotechnic munitions often contain metals burned to produce light and smoke. As pyrotechnics and smoke munitions are frequently used on Army training lands, metals deposited by these rounds may build up in the soils and may need to be sampled as part of the MMRP. The deposition of metals from these rounds, however, has never been evaluated. To fill this data gap, this study focused on field testing of four commonly used pyrotechnic devices; M18 Green Smoke Hand Grenade, M21 Flash Artillery Simulator, M117 Booby Trap Flash Simulator, and M127A1 White Parachute Illumination Signal and examined 1) what metals are most commonly used in Army pyrotechnics, 2) how metals are deposited and the associated residue mass, and 3) approaches for determining the residues left by these devices.

2 Background

Pyrotechnics are devices providing an effect such as heat, light, smoke, or sound (Bailey and Murray 1989, Conkling 1985). Development of military pyrotechnics began during World War I (WWI), adopting formulations from commercial fireworks (Faber 1919). Faber is considered the "father" of military pyrotechnics because he and his students developed many of the modern equivalents. Brevet Major T.T. S. Laidley (Faber 1919) published the first US Army Ordnance Manual describing pyrotechnics in 1861.

Pyrotechnics consist of a fuel, an oxidizer, and additives to provide the desired special effect. Organic compounds present in the filler are combusted, presumably to carbon dioxide, water, and soot. The combustion process heats the metals to their excited states such that their characteristic colors are produced. Typically used metal powders are aluminum, antimony, barium, boron, chromium, cerium, copper, iron, lead, magnesium, manganese, titanium, tungsten, zinc, and zirconium in the size range of 5 to 1,000 micrometers. Inorganic non-metals also present in some pyrotechnic formulations include boron, carbon, silicon, sulfur, or phosphorous. The oxidizers are salts of chlorates, chromates, dichromates, halocarbons, iodates, nitrates, oxides, and perchlorates (Bailey and Murray 1989, Conkling 1985).

It is important to note which metals are not present in pyrotechnics as some of these are of environmental interest: arsenic, beryllium, cadmium, cobalt, mercury, molybdenum, nickel, thallium, tin, and vanadium (MIDAS 2009, US Army 1963, Bebie 1943). According to Faber (1919), arsenic was used in tracer smoke during WW I but this review found no additional information. In addition, the US Army (1963) identified lithium, lithium nitrate ($LiNO_3$), and lithium perchlorate ($LiClO_4$) as oxidizers added to red burning compositions, but none of the pyrotechnics reviewed contained lithium based on the US Army's Munition Items Disposition Action System (MIDAS) database (MIDAS 2009). Perhaps, lithium was used pre-1960, but no documentation was found. In addition, molybdenum and nickel were identified as fuels for some pyrotechnics (US Army 1963) but none of the current munitions described by MIDAS document their use. Hence, these metals were not included as contaminants of potential concern (COPC).

2.1 Approach

The MMRP is interested in munition residues, deposited from the 1940s to 1980s. Ideally, pyrotechnic devices from that time period would be tested. Although some munitions are retained within the military inventory for considerable lengths of time, this is not the case for pyrotechnics. Both because of a short shelf life (primarily caused by degradation by moisture) and the increased tempo of military training, devices older than ten years are no longer in the inventory.

Because the tests had to be conducted with items in the current military inventory, the information desired was 1) what pyrotechnics are most widely used; 2) what metals are present in the pyrotechnic filler; 3) what metals were contained in the older pyrotechnics; and 4) have the metals changed.

Although various reports (Bailey and Murray 1989, Conklin 1985, Ellern 1961) provide some information about pyrotechnic composition, little information is available regarding the type or number of rounds fired prior to 1990. Consequently, the pyrotechnic devices currently used for military training have been identified and it has been assumed that their historical usage and formulations were similar. Appendix A lists the pyrotechnics used from 2005 to 2008 at all Alaska ranges and from 1911 to 1999 at Camp Edwards, Massachusetts (USACE 1999). Appendix A also lists munition items procured by the US Army for the period 2007 to 2009.

Since the attacks of September 11, 2001, the training tempo at ranges has increased significantly from the rate in the 1970s to 1990s. However, the training levels associated with World War II (WWII), Korean, and Vietnam conflicts were elevated as compared to periods when major military conflicts were absent. Therefore, the use of recent records seems a reasonable approximation of past use.

Anthropogenic metal concentrations in soil are likely to be screened against US Environmental Protection Agency (USEPA) Region IX residential Preliminary Remediation Goals (PRGs) or similar regulatory guidelines. Thus, the PRGs, as well as range of background values, are provided in Table 1 for the metals of interest. An assessment by Ogden (2000) suggests the following metals are COPC and should be considered by the MMRP: aluminum, antimony, barium, boron, copper, lead, manganese, and zinc, which encompasses some of the known metals in pyrotechnics. There are no regulatory standards for cerium or zirconium, although these compounds are used in some pyrotechnic devices.

Table 1. Pyrotechnic metals of interest, USEPA Region IX residential Preliminary Remediation Goals, and representative background values.

Analyte	USEPA Region IX PRG (mg/kg) [1]	Common Soil Ranges (mg/kg)[2]	Common Soil Ranges (mg/kg)[3]	Arithmetic Mean Soil Values (mg/kg)[4]	Crustal Average (mg/kg)[5]	Soil Partitioning Coefficients (K_d's) (ml/g)
Aluminum	7,700	10,000-300,000	NA	72,000	82,300	1,500[b]
Antimony	3.1	NA	0.05-4	0.66	0.2	150[a]
Barium	1,500	100-3,000	200-1,500	580	425	50[b]
Boron	1,600	NA	NA	NA	NA	NA
Cerium	NA	NA	NA	NA	NA	NA
Chromium	130	1-1,000	10-100	54	100	30[a]
Cobalt	233	NA	NA	NA	NA	NA
Copper	310	2-100	5-100	25	55	3.5[b]
Iron	5,500	NA	NA	26,000	56,300	NA
Lead	400	2-200	10-30	19	12.5	1,600[a]
Magnesium	NA	600-6,000	NA	9,000	23,300	NA
Manganese	180	20-3,000	50-1,500	550	950	758[a]
Molybdenum	391	NA	NA	NA	NA	NA
Potassium	NA	400-30,000	NA	15,000	20,900	NA
Sodium	NA	NA	NA	12,000	23,600	NA
Titanium	14,000	NA	NA	NA	NA	NA
Tungsten	NA	NA	NA	NA	1.3[6]	18-477[c]
Zinc	2,300	10-300	20-110	60	70	1,300[a]
Zirconium	NA	NA	NA	NA	NA	NA

NA – not applicable, [a]Sheppard and Thiboult 1990, [b]Baes *et al.* 1984, [c]Clausen *et al.* 2009a
1 USEPA 2009, [2] Lindsay 1979, [3] Kabata-Pendias and Pendias 1984,
[4] Shacklett and Boerngen 1984, [5] Taylor 1964.
[6] Clausen and Korte 2009b (background value)

2.2 Ground Discharged Devices

The ground discharged munitions include a variety of signal smokes, smoke pots, and simulators (Table 2). The M18 Green Smoke Hand Grenade, M21 Flash Artillery Simulator, and M117 Booby Trap Flash Simulator are the ground discharged devices studied.

Table 2. Types of ground discharged pyrotechnics and military identification numbers.

Type of Pyrotechnic	Military Identification
Signal smokes	M18, M82, M83
Smoke pots	M1, M3, M8
Simulators	M21, M25, M30, M34, M35, M74, M115A2, M116A1, M117, M118, M119, M311

The ground discharge devices are typically used in areas referred to by the military as Training Areas. The Training Areas typically span an area of a few hundred to several thousand acres. Training Areas are used for mounted and dismounted training. Live fire ammunition is not typically used in these areas, although pyrotechnic devices such as smokes are permissible. US Army (1974) differentiates between markers and signals which can emit either smoke or light—flare with length of burning time is the key difference. Markers have longer burn times than signals and are generally smaller than flares (see Section 2.3.3).

2.2.1 Smoke Hand Grenades

Smoke hand grenades are used for screening or signaling and emit 50 to 90 seconds and can be thrown 30 meters by an average soldier (US Army 1967). The smoke grenade offers a realistic replication that can be used to train ground-to-ground or ground-to-air signaling, target or landing zone marking or unit movement screening. The smoke grenade casing is of a metal composition. Current range management practices require turn in of the pin and the spent grenade casing.

The smoke grenades can emit a variety of colors and include metals for infrared screening. The typical metals used in smoke grenades are iron, magnesium, and potassium. Other metals present in smaller amounts are barium, lead, and zirconium. Exceptions are the M1 and M3 smoke devices which principally consist of aluminum and titanium. The colored smoke is generated by the combustion of various dyes. According to Ellern (1961), colored smoke from the WWII era consisted of dyes with no metal constituents. .Colored smoke munitions from the Vietnam War era, however, contained barium nitrate($Ba(NO_3)_2$), antimony trisulfide (Sb_2S_3), potassium chlorate, zirconium, carbon black, sodium nitrate, and magnesium carbonate in addition to the dyes and Hexachloroethane (HC). Kitchens et al (1978) identified all of these metals as COPCs

Other devices identified in US Army (1974) that discharge smoke include the XM116 White Signal Smoke and the AN-M8 HC Smoke Hand Grenade, which were identified as being used at Camp Edwards (Appendix A). The AN-M8 HC has an ignition mixture containing iron oxide, titanium, and zirconium (US Army, 1994a). Prior to WWII these devices used zinc chloride ($ZnCl_2$) (US Navy 1947). During WWII white smokes consisted of carbon tetrachloride (CCl_4), aluminum, and zinc oxide (Hardt 2001). Subsequently, the filler formula was changed to HC, zinc oxide (ZnO), and ammonium perchlorate (NH_4ClO_4). Current HC mixtures contain zinc oxide, HC, and aluminum chloride ($AlCl_3$) (Ellern 1961). The Army procured AN-M8 HC grenades as late as 2008 (US Army, 2008) but the HC component is thought to be carcinogenic. Thus, they were replaced by the less harmful M83 (US Army, 2000).

2.2.2 Battlefield Effect Simulators

Battlefield effect simulators such as M21, M25, M30, M34, M35, M74A1, M110, M115A2, M116A1, M117, M118, M119, M311, and EX1 Mod 0 mimic the sound of shells in flight, ground burst explosions, or grenade detonations. Their greatest use is at the combined training centers and infiltration courses at troop training sites. They can also be used in designated Training Areas. These devices are all activated on the ground surface.

The casing material for battlefield effect simulators consist of paper, which is either consumed in the detonation or scattered on the ground surface. Historically, black powder was used to provide the flash and smoke with this formulation phased out in the 1950s. Black powder consists primarily of charcoal, sulfur, and potassium nitrate (KNO_3) (also known as Saltpeter). Metals present in current-day simulators can include aluminum, antimony, barium, boron, cerium, copper, iron, lead, magnesium, potassium, sodium, and zinc but vary significantly by device. Flash and sound are usually generated with aluminum and/or magnesium, potassium perchlorate ($KClO_4$), and sometimes antimony sulfide (Sb_2S_3) (Bailey and Murray, 1989). Occasionally zirconium is used to provide the flash (Hardt 2001).

2.3 Air Launched Devices

Air launched smoke devices include grenades, mortar and artillery fired smokes, air launched flares, and projectile illumination rounds. The latter are fired from 40, 60, 81, and 120mm mortars and 105 and 155mm artillery weapon systems (Table 3).

Table 3. Types of air launched pyrotechnics and military identification numbers.

Type of Pyrotechnic	Military Identification
Grenades	M82, M90, M167, L8A3
Mortar and artillery fired smokes	M60, M60A1, M60A2, M60E1, M84, M84A1, M84B1, M116, M116B1, M301A, M680, XM929
Air launched flares	H183, M19A1, M19A2, M49, M49A1, M116A1, M125A1, M126A1, M127, M127A1, M158, M159, M195
Projectile illumination rounds	M48, M83A1, M301A, M314, M721, M767, M816, M853, M983, M1105, XM93

2.3.1 Launched Smoke Grenades

In addition to the launched smoke devices, Kitchens et al. (1978) identified the M176 and M226 signal smoke launchers as pyrotechnics used during the Vietnam War period. Also, the US Army (1974) lists the M62 Red Signal Smoke Grenade as being fired from M7 Rifle Grenade Launcher attached to a M14 Rifle. The device produced six red smoke streamers of 76 m in length, which persisted for 20 sec in a wind of 5 mph. The M62 and M226 devices are not listed in the MIDAS database suggesting it was phased out of service sometime after 1974. Other apparently discontinued devices include the XM144 Ground Signal series developed to replace the M125 and T133 Signal Series (US Army 1974). Similarly, the XM150 and XM153 are no longer in service. The XM150 Smoke Parachute reached a height of 230 m and emanated smoke for 1 minute when deployed whereas the XM153 Smoke Streamer issued smoke for 7 to 8 seconds (Lopatin 1963).

2.3.2 Smoke Fired Projectiles from Mortars and Artillery

The smokes used by the 40, 81, and 120mm mortars include the following; M680 40mm White Smoke, M301A 81mm White Phosphorous Smoke, and XM929 120mm White Phosphorous Smoke. The smokes used by the 105 and 155mm artillery pieces include the following: M60, M60A1, M60A2, and M60E1 105 mm White Phosphorous Smoke, M84, M84A1, M84B1 105 mm HC Smoke, and M116 and M116B1 155mm Red Smoke. Shinn *et al* (1985) indicate that the mortar and artillery fired smoke devices would affect an area less than 3 acres. Dauphin and Doyle (2001) indicate the dud and low order rate for White Phosphorous and Red Phosphorous smoke rounds are 3.5 and 0.1 percent, respectively.

The metals present in the mortar and artillery launched smokes vary considerably by device but in general include antimony, barium, lead, and potassium. Other metals that can be present in these devices include aluminum and boron.

2.3.3 Flares and Stars

The flares used by the military include the M19A1 and M19A2 Signal Illumination Grenade Parachute, M49A1 Surface Trip Flare, M116A1 Signal Hand Grenade, M125A1 Signal Green Star Cluster, M126A1 Signal Red Parachute Flare, M127 and M127A1 Signal White Parachute, M158 Signal Red Star Cluster, M159 Signal White Star Cluster, M195 Green Parachute Signal Flare, and M257 Rocket Flare. The M127A1 Signal White Parachute was studied as part of this project. The M117 to M127 Series have been used since the early 1940's and the formulation has been largely unchanged (Ellern 1961).

Stars are similar to flares except for the duration of the light and luminosity (Hardt 2001). Strontium is the element providing red coloration and barium green. Ellern (1961) suggests magnesium powder (major fuel), strontium or barium (coloration and oxidizer), Hexachlorobenzene (C_6Cl_6), or polyvinyl chloride (chlorine donors and color enhancers), and potassium perchlorate (additional oxygen and chlorine source as well as burn rate regulator) are the major constituents indicating the formulation has not changed over the last half century (Ellern 1961).

In general, all of the flares are initiated by hitting the base on a hard surface. The flare climbs to a maximum elevation of approximately 60 m depending on weather conditions. Flares with an attached parachute design descend slowly and have the potential to drift further away from the initiation point than non-parachute devices. The devices are typically used for signaling or providing illumination of targets.

2.3.4 Illumination Projectiles

This category of devices includes illumination projectiles or candles used with mortar and artillery weapon systems. Illumination candles provide a minimum of 0.05 to 10 foot candles of white light up to 2 million candlepower for at least 30 seconds and up to 2 to 3 minutes (US Army 1967). Magnesium oxide (MnO) and sodium nitrate ($NaNO_3$) are the primary constituents (Hardt 2001). Older formulations sometimes contained barium nitrate with sodium oxalate ($Na_2C_2O_4$) (Hardt 2001). Strontium nitrate ($Sr(NO_3)_2$), potassium nitrate, and potassium chlorate were also sometimes used with these older mixtures (US Army 1974). Dauphin and Doyle (2001) indicate that the overall dud rate for illumination projectiles is 2.1 percent and the low order rate is 0.7 percent.

2.3.5 Other Devices

2.3.5.1 Photoflash Devices

Hardt (2001) reported that photoflash devices were used by the military prior to the 1970s. Ellern (1961) indicates these devices were introduced during WW I. These devices include the M112, M112A1, M123, and M123A1 photoflash cartridges and M120 and M120A1 photoflash bombs. The devices were primarily dropped from aircraft at mid to low altitudes. Barium nitrate, potassium perchlorate, and aluminum powder were used in these devices. According to US Army (1977), these devices contained 0.2 to 2 kg of pyrotechnic photo flash powder. These devices were developed circa 1925 and by 1930 consisted of a formulation of 34% magnesium, 26% aluminum, and 40% potassium perchlorate (US Army 1967). Later barium nitrate was added as an oxidizer. With the advent of digital photographic technology photoflash pyrotechnic devices are no longer used by the US military.

2.4 Tested Devices

2.4.1 M18 Green Colored Smoke Grenade

The ground discharged device evaluated in this study was the M18 green colored smoke grenade (Figure 1). The Army procured 126,000 of these devices in FY09 and used them at both Alaska Ranges (Fort Richardson and Fort Wainwright) and the Massachusetts Military Reservation (MMR) (Appendix A). This usage is likely similar to usage at other military installations. The M18 colored smoke hand grenade is effective as a ground-to-ground or ground-to-air signaling device, target or landing zone marking device, or for screening unit movements by putting out clouds of dense smoke. The grenade can be filled with any one of four smoke colors: green, yellow, red, and violet. Each grenade emits smoke for 50 to 90 seconds and can be thrown 30 meters by an average soldier. The smoke plume can reach a height of 30 m depending on the wind conditions. Low wind will result in greater height and less dispersion whereas greater wind velocities will result in lower maximum smoke plume height and greater downwind dispersion. Dauphin and Doyle (2001) state the dud rate for colored smoke munitions is 9.7% with a low-order detonation rate of 7.0%.

The principal components of the smoke, by mass, are potassium chlorate ($KClO_3$), magnesium carbonate ($MgCO_3$), and potassium nitrate (MIDAS 2009). The other metals of interest for this particular device are barium, iron, lead, magnesium, manganese, potassium, titanium, and zirconium present at a mass of less than 1 gram (Table 2). The ignition mixture of the M18 Smoke Grenade

contains iron oxide, titanium, and zirconium (USACE 1999). US Army (1974) suggests the principal metal is in the form of potassium perchlorate, which suggests the formulation changed sometime prior to the early 1970s to the current formulation.

A risk evaluation was conducted for Camp Edwards, Massachusetts that included metals in soil and was based on a residential land use surface exposure risk scenario using USEPA Region IX preliminary remediation goals [PRGs] (Ogden, 2000). Metals contained in smokes that are COPCs according to this assessment are barium, lead, and manganese. The highest concentration of any COPC is lead chromate, although the total mass is less than ½ gram per individual device (Table 4). Potassium and magnesium are not COPCs.

Figure 1. Example of M18 Green Signal Smoke Hand Grenade.

Table 4. Summary of metal constituents for pyrotechnic devices tested.

Usage		Signal Smoke	Flash Arty Simulator	Booby Trap Simulator	Signal White Parachute
Color of Smoke		Green	NA	NA	NA
Type of Device		Grenade	Ground	Ground	Air Launched
Military Designation		M18	M21	M117	M127A1
DODIC Number		G940	L602	L598	L312
Nomenclature (Material)	CAS #	Mass (g)	Mass (g)	Mass (g)	Mass (g)
Aluminum	7429-90-5	NA	9.56	NA	NA
Aluminum Powder	7429-90-5	NA	NA	NA	0.004
Antimony Sulfide	1345-04-6	NA	NA	0.645	0.009
Barium Chromate	10294-40-3	0.030	NA	NA	0.321
Barium Nitrate	10022-31-8	0.002	26.4	NA	0.082
Cerium	none given	NA	0.002	NA	NA
Chromium Oxide	1308-38-9	NA	NA	NA	0.015
Cobalt Naphthenate	61789-51-3	NA	NA	NA	0.017
Copper Oxide Black	1317-38-0	NA	1.32	NA	NA
Iron	7439-89-6	NA	0.053	NA	0.025
Iron Oxide	1317-61-9	0.008	NA	NA	NA
Lead Chromate	7758-97-6	0.318	NA	NA	NA
Lead Mononitroresorcinate	51317-24-9	NA	0.023	NA	NA
Lead Peroxide	1309-60-0	NA	0.002	NA	NA
Lead Styphnate	15245-44-0	NA	NA	NA	0.023
Lead Thiocyanate	592-87-0	0.010	NA	NA	NA
Magnesium	7439-95-4	NA	NA	NA	55.0
Magnesium Carbonate	13717-00-5	55.4	NA	NA	NA
Magnesium Powder	7439-95-4	NA	NA	0.425	NA
Manganese Powder	7439-96-5	0.252	NA	NA	NA
Molybdenum Trioxide	1313-27-5	NA	NA	NA	0.023
Potassium Chlorate	3811-04-9	79.9	0.002	0.646	NA
Potassium Nitrate	7757-79-1	2.95	NA	0.791	27.6
Potassium Perchlorate	7778-74-7	0.009	NA	1.25	0.065
Red Phosphorus	7723-14-0	NA	NA	0.326	NA
Sodium Nitrate	10042-76-9	NA	NA	NA	24.7
Titanium Powder	7440-32-6	0.021	NA	NA	NA
Tungsten or Tungsten Powder	7440-33-7	NA	NA	NA	0.182
Zinc	7440-66-6	NA	0.031	NA	0.842
Zirconium	7440-67-7	0.020	NA	NA	0.052
Zirconium Hydride	7704-99-6	NA	NA	NA	0.020

NA – not applicable, Data obtained from MIDAS database (MIDAS 2009).

2.4.2 M21 and M117 Simulators

Two simulators were tested as part of this study, the M21 flash artillery battlefield simulator (Figures 2 and 3) and the M117 booby trap simulator (Figure 4). The M21 and M117 simulators were used in training at MMR (Appendix A). In FY09, 59,000 M117 simulators were procured by the Army (Appendix A). In 2002, more than 60,000 M21 devices were fired at training facilities across the country (Von Stackleberg *et al.* 2006).

Figure 2. Example of M21 flash artillery simulator.

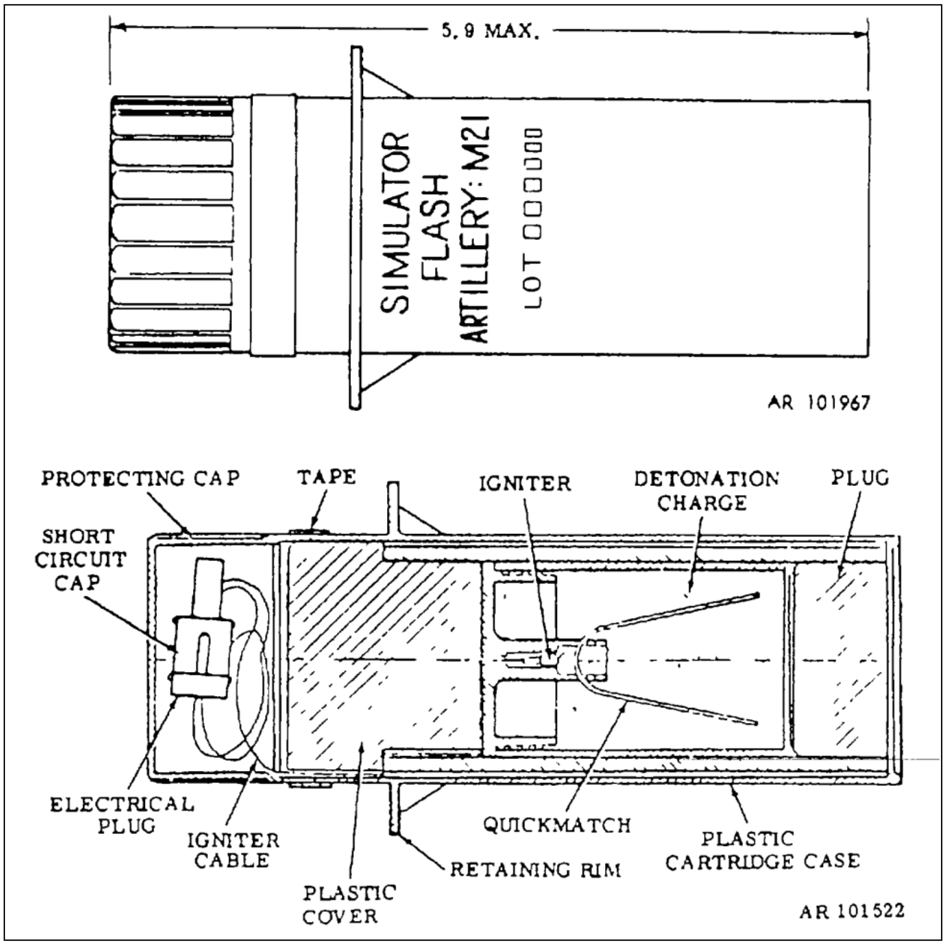

Figure 3. Diagram of M21 flash artillery simulator.

Figure 4. Example of M117 booby trap simulator.

The M21 simulates the sound and, optionally, the flash and smoke characteristic of an artillery firing signature. This device burns instantaneously after the flash powder charge is ignited by an electrical signal (US Army 1994a). Flash powder compositions can vary but typically include potassium perchlorate as the oxidizer and aluminum powder as the metallic fuel. Sometimes sulfur is included to increase the sensitivity. Previous formulations substituted potassium permanganate ($KMnO_4$) for potassium perchlorate. The M117 produces a loud report and flash when triggered by a trip wire.

The primary filler constituents of the M21 are aluminum, barium nitrate, and copper oxide black (Table 2). Secondary metal constituents with a mass of less than 1 g per device include cerium, iron, lead, potassium, and zinc. The two principal anions associated with the metals are nitrate and chlorate.

The M117 produces a loud report and flash when the simulator is triggered by a trip wire and fired. These simulators teach troops installation, detection, and caution by simulating booby traps a soldier might encounter on the battlefield. Although not shown to have been used in Alaska for training (Appendix A) large quantities were procured by the Army (Appendix A). These devices have been used since WWII (Ellern 1961). Von Stackleberg *et al.* (2006) reports 2,078 M117 Booby Trap Simulators were fired in 2002.

The principal metal of interest in the M117 (Figure 5) is antimony from antimony sulfide (Table 2). Prior to the 1980s, the constituents in the whistling booby trap simulators included 73% potassium perchlorate, 24% gallic acid, and 3 % red gum (McIntyre 1980). Whereas the booby-trap flash simulators contained 17% magnesium, 33% antimony sulfide, and 50% potassium perchlorate (US Army, 1974, Ellern, 1961).

The primary filler constituent in the M117 is potassium perchlorate (Table 2). The principal metals in the M117 device are antimony, manganese, and potassium. Red phosphorous is also present along with the anions of chlorate, perchlorate, and nitrate. Other metals of interest are lead and cerium.

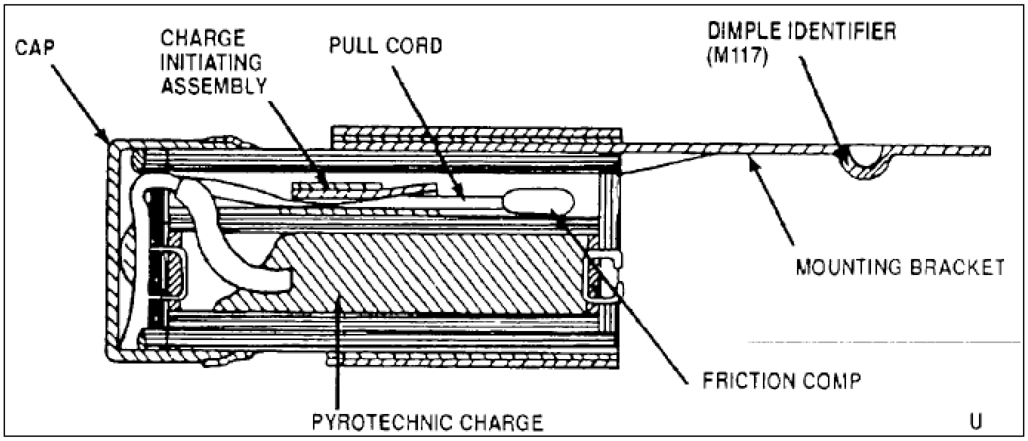

Figure 5. Schematic diagram of the M117 Booby Trap Simulator (US Army 1994b).

2.4.3 M127A1 Illumination White Parachute Flare

The illumination white parachute flare M127A1 was the air-launched device tested as part of this study (Figure 6). The device is primarily used for surface-to-air distress signaling, location signaling between troop emplacements, and battlefield illumination at night. The M127A1 Signal is a white star illuminant parachute suspended and propelled by a fin-stabilized rocket motor propulsion assembly contained in a ten-inch, hand-held aluminum launching tube weighing 0.5 kg. The rocket assembly reaches an altitude of 200 m before the initiating charge ignites the white star illuminant and the assembly parachutes to the ground and burns for 30 seconds at 125,000 candlepower (US Army 1977). The M127A1 is used heavily in training with hundreds to thousands deployed per military installation in 2002 (Von Stackleberg *et al.* 2006).

This device has been used at the Alaska Ranges and MMR with 83,000 procured by the US Army in FY09 (Appendix A). The principal constituents in the flare are magnesium, potassium nitrate, and sodium nitrate (Table 2). The primary metals in the M127A1 also include barium and zinc. Other metals present include aluminum, chromium, cobalt, iron, lead, molybdenum, tungsten, and zirconium. The propellant used in the flare is black powder.

Figure 6. Example of M127A1 signal illumination ground white star parachute.

3 Methods

Quantifying the amount of metal deposited from pyrotechnic devices is difficult because the mass deposited is low relative to the background soil level. Furthermore, pyrotechnics vary in how they are deployed. Some, such as many of the smoke rounds, are set on the ground where they burn while others, such as the illumination flares, are fired into the air where they burn at altitude and disperse their metals over large areas. In addition, the loading of metals from previous range activities makes calculation of residue mass in soil difficult (Walsh *et al.* 2007).

To quantify the metal deposition from these rounds, multiple rounds of each pyrotechnic were detonated over a clean snow surface and the residue deposited on the snow and in trays was collected. The basis for this approach is previous work conducted to determine energetic loading rates on snow (Walsh *et al.* 2005, Hewitt *et al.* 2003, Jenkins *et al.* 2002).

Initially it was thought that an air dispersion model such as SCIPuff was needed to predict the spatial distribution and mass of metals residues. However, the spatial distribution of detonation residues, black soot or green dye, was easily visible on the snow surface. Therefore, the SCIPuff software program was not used. Snow sampling was followed later in the spring with soil sampling in the same area that snow samples were collected.

3.1 Pyrotechnic Detonation Tests

The detonation tests took place on 2, and 4-5 February 2010 at Camp Ethan Allen Firing Range 4-1 and 4-3. The weather conditions at the time of the tests were a slight overcast with calm to light winds and a temperature (°F) in the low teens each day. The snow cover was thin and in some areas absent. In the location of the tests, the snow depth varied from 5 to 10 cm. The total number of devices tested is listed in Table 5.

Table 5. Pyrotechnic devices tested on snow.

Name		Number Tested	Military ID	NSN
Hand Grenade Green Smoke	G	32	M18	1330-00-289-6851
Simulator Booby Trap Flash	G	50	M117	1370-00-028-5256
Simulator Flash Artillery Simulator	G	36	M21	1370-01-034-1397
Signal Illumination Ground Parachute	A	48	M127A1	1370-00-753-1859

NSN – national stock number, G= ground discharge device,
A= air launched device

3.1.1 M18 Green Colored Smoke Grenade

Three tests were conducted where the M18 green smoke hand grenade was tossed into a soft snow bank. The heat of combustion resulted in the smoke grenades melting the snow and sinking further below the snow surface. Very little smoke was emitted into the atmosphere with most of the smoke sorbed into the snow (Figure 7). A small portion of the snow melted and then refroze. All of the-green stained snow was dug up and collected in large plastic bags. The sample identification corresponding to these tests were CEA4-3 #1-3 (Table 4). Because of the volume of snow collected, two bags denoted A and B were filled for each test.

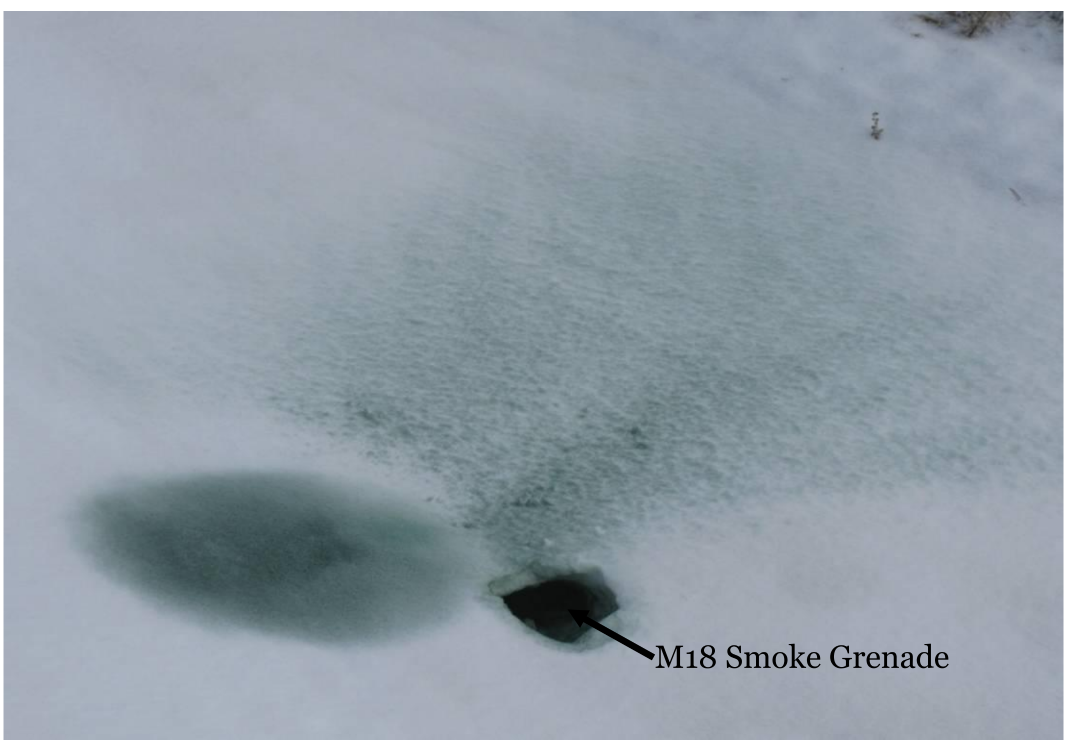

Figure 7. Residue from buried M18 Green Signal Smoke Hand Grenade on snow.

A second test was conducted where the smoke grenades were tossed on top of a thin snow surface and they discharged smoke while lying on their side (Figure 8). The entire area of green stained snow was collected, e.g. sample identification CEA4-3 #4-6 (Figure 9, Table 6). As can be seen in Figures 8 and 9 a considerable amount of green snow staining occurred next to the nozzle of the smoke grenade. However, a portion of the smoke was dispersed into the light wind. Two sample trays were also placed downwind near the detonation of the smoke grenade as part of the CEA4-3 #4-6 tests. The samples have sample identification numbers of CEA4-3 #7 and 8.

Table 6. Pyrotechnic devices tested and corresponding snow sample identification.

Sample ID	Range	Comments	Nomenclature	Number Increments	Snow Weight (g)	Field Sample Collection Date
CEA 4-3 #1	4-1	Test 1. Buried smoke grenade, complete plume collection, 2 bags	M18 Green Smoke Hand Grenade	All	13,823.8	2/2/10
CEA 4-3 #2	4-1	Test 2. Buried smoke grenade, complete plume collection, 2 bags	M18 Green Smoke Hand Grenade	All	13,400.3	2/2/10
CEA 4-3 #3	4-1	Test 3. Buried smoke grenade, complete plume collection, 2 bags	M18 Green Smoke Hand Grenade	All	12,839.3	2/2/10
CEA 4-3 #4	4-1	Test 4. On surface smoke grenade, complete plume collection, roughly 2 x 1 m	M18 Green Smoke Hand Grenade	All	1465.3	2/2/10
CEA 4-3 #5	4-1	Test 5. On surface smoke grenade, complete plume collection, roughly 2 x 1 m	M18 Green Smoke Hand Grenade	All	3014.2	2/2/10
CEA 4-3 #6	4-1	Test 6. On surface smoke grenade, complete plume collection, roughly 2 x 1 m	M18 Green Smoke Hand Grenade	All	6944.0	2/2/10
CEA 4-3 #7	4-1	Tray sample during Test 4.	M18 Green Smoke Hand Grenade	NA	NA	2/2/10
CEA 4-3 #8	4-1	Tray sample during Test 5.	M18 Green Smoke Hand Grenade	NA	NA	2/2/10
CEA 4-3 #9	4-1	Background snow sample collected in area near entrance to range 4-3, near building.	Background	50	1634.2	2/2/10
CEA 4-3 #10	4-1	Background snow sample collected in area near entrance to range 4-3, near building.	Background	50	1744.5	2/2/10
CEA 4-3 #11	4-1	Background snow sample collected in area near entrance to range 4-3, near building.	Background	50	3147.0	2/2/10
CEA 4-3 #12	4-1	Test 1. MI snow sample following detonation of 10 simulators. Rep 1.	M21 Flash Artillery Simulator	56	1995.9	2/2/10
CEA 4-3 #13	4-1	Test 1. MI snow sample following detonation of 10 simulators. Rep 2.	M21 Flash Artillery Simulator	70	1595.7	2/2/10
CEA 4-3 #14	4-1	Test 1. MI snow sample following detonation of 10 simulators. Rep 3	M21 Flash Artillery Simulator	75	1005.0	2/2/10
CEA 4-3 #15	4-1	Test 1. Tray sample closest to detonation	M21 Flash Artillery Simulator	NA	NA	2/2/10
CEA 4-3 #16	4-1	Test 1. Tray sample middle downgradient location	M21 Flash Artillery Simulator	NA	NA	2/2/10
CEA 4-3 #17	4-1	Test 1. Tray sample furthest downgradient location	M21 Flash Artillery Simulator	NA	NA	2/2/10

Sample ID	Range	Comments	Nomenclature	Number Increments	Snow Weight (g)	Field Sample Collection Date
CEA 4-3 #20	4-1	Test 1. Rinseate from tray #15	M21 Flash Artillery Simulator	NA	NA	2/2/10
CEA 4-3 #21	4-1	Test 1. Rinseate from tray #16	M21 Flash Artillery Simulator	NA	NA	2/2/10
CEA 4-3 #22	4-1	Test 1. Rinseate from tray #17	M21 Flash Artillery Simulator	NA	NA	2/2/10
CEA 4-3 #25	4-1	Test 1. Rinseate from smoke grenade cartridge	M18 Green Smoke Hand Grenade	NA	NA	2/2/10
CEA 4-3 #26	74	MI snow sample near 8 flares burned 2m off ground, Test 1, Rep 1	M127A1 Signal Illumination Parachute	50	1324.0	2/4/10
CEA 4-3 #27	74	MI snow sample near 8 flares burned 2m off ground, Test 1, Rep 2	M127A1 Signal Illumination Parachute	50	587.1	2/4/10
CEA 4-3 #28	74	MI snow sample near 8 flares burned 2m off ground, Test 1, Rep 3	M127A1 Signal Illumination Parachute	50	1276.7	2/4/10
CEA 4-3 #29	74	MI 10m downgradient snow sample of Test 1, radius 3x6m, Rep 1	M127A1 Signal Illumination Parachute	50	914.0	2/4/10
CEA 4-3 #30	74	MI 10m downgradient snow sample of Test 1, radius 3x6m, Rep 2	M127A1 Signal Illumination Parachute	45	602.0	2/4/10
CEA 4-3 #31	74	MI 10m downgradient snow sample of Test 1, radius 3x6m, Rep 3	M127A1 Signal Illumination Parachute	55	1157.4	2/4/10
CEA 4-3 #32	74	All residue immediately beneath burning of 8 flares, Test 1	M127A1 Signal Illumination Parachute	All	4845.2	2/4/10
CEA 4-3 #33	74	MI snow sample near 8 flares burned 2m off ground, Test 2, Rep 1	M127A1 Signal Illumination Parachute	50	1466.8	2/4/10
CEA 4-3 #34	74	MI snow sample near 8 flares burned 2m off ground, Test 2, Rep 2	M127A1 Signal Illumination Parachute	50	558.8	2/4/10
CEA 4-3 #35	74	MI snow sample near 8 flares burned 2m off ground, Test 2, Rep 3	M127A1 Signal Illumination Parachute	50	1089.2	2/4/10
CEA 4-3 #36	74	MI snow sample 10m downwind of 8 flares, 3 x 6m, Test 2, Rep 1	M127A1 Signal Illumination Parachute	50	997.1	2/4/10
CEA 4-3 #37	74	MI snow sample 10m downwind of 8 flares, 3 x 6m, Test 2, Rep 2	M127A1 Signal Illumination Parachute	45	1060.1	2/4/10
CEA 4-3 #38	74	MI snow sample 10m downwind of 8 flares, 3 x 6m, Test 2, Rep 3	M127A1 Signal Illumination Parachute	50	971.8	2/4/10
CEA 4-3 #39	74	All residue beneath burning of 8 flares, Test 2	M127A1 Signal Illumination Parachute	All	3725.7	2/4/10
CEA 4-3 #40	74	Tray residue beneath 1 flare. Test 3.	M127A1 Signal Illumination Parachute	NA	NA	2/4/10
CEA 4-3 #41	74	Tray residue beneath 2 flares. Test 4	M127A1 Signal Illumination Parachute	NA	NA	2/4/10

Sample ID	Range	Comments	Nomenclature	Number Increments	Snow Weight (g)	Field Sample Collection Date
CEA 4-3 #42	4-1	Test 1, Detonation of 10 devices. Complete snow collection, bag #1	M117 Booby Trap Flash Simulator	All	5246.2	2/4/10
CEA 4-3 #43	4-1	Test 1, Detonation of 10 devices. Complete snow collection, bag #2	M117 Booby Trap Flash Simulator	All	5844.5	2/4/10
CEA 4-3 #44	74	Background snow sample, Range 74	Background	50	2405.1	2/4/10
CEA 4-3 #45	4-1	Test 1, Detonation of 10 devices. Complete snow collection, consisting of 3 bags	M117 Booby Trap Flash Simulator	All	1454.9	2/4/10
CEA 4-3 #46	4-1	Test 2, Detonation of 10 devices. Complete snow collection, consisting of 3 bags	M117 Booby Trap Flash Simulator	All	8,673.5	2/4/10
CEA 4-3 #47	4-1	16 Green smoke grenades detonated upright in holders, MI snow sample. Test 7, Rep. 1.	M18 Green Smoke Hand Grenade	57	1547.5	2/4/10
CEA 4-3 #48	4-1	16 Green smoke grenades detonated upright in holders, MI snow sample. Test 7, Rep. 2	M18 Green Smoke Hand Grenade	47	648.3	2/4/10
CEA 4-3 #48	4-1	16 Green smoke grenades detonated upright in holders, MI snow sample. Test 7, Rep. 3	M18 Green Smoke Hand Grenade	42	1284.3	2/4/10
CEA 4-3 #50	4-1	Test 7, Snow particles in a jar	M18 Green Smoke Hand Grenade	NA	NA	2/4/10
CEA 4-3 #51	4-1	10 M21s detonated Test 2, MI snow sample, Rep 1	M21 Flash Artillery Simulator	54	1931.2	2/5/10
CEA 4-3 #52	4-1	10 M21s detonated Test 2, MI snow sample, Rep 2	M21 Flash Artillery Simulator	57	2347.3	2/5/10
CEA 4-3 #53	4-1	10 M21s detonated Test 2, MI snow sample, Rep 3	M21 Flash Artillery Simulator	75	3381.2	2/5/10
CEA 4-3 #54	4-1	10 M21s detonated Test 2, Snow particles in jar	M21 Flash Artillery Simulator	NA	NA	2/5/10
CEA 4-3 #55	4-1	10 M21s detonated Test 3, MI snow sample, Rep 1	M21 Flash Artillery Simulator	50	2281.1	2/5/10
CEA 4-3 #56	4-1	10 M21s detonated Test 3, MI snow sample, Rep 2	M21 Flash Artillery Simulator	50	2667.8	2/5/10
CEA 4-3 #57	4-1	10 M21s detonated Test 3, MI snow sample, Rep 3	M21 Flash Artillery Simulator	50	3785.8	2/5/10

All – indicates the entire volume of stained snow was removed. MI – multi-increment.

Rep. - replicate

Figure 8. Demonstration of sideways test of M18 Green Signal Smoke Hand Grenades.

Figure 9. Residue on snow from detonation of M18 Green Signal Smoke Hand Grenade from sideways test.

A final test consisted of igniting the remaining 16 green smoke grenades in an upright position (Figures 10 and 11) using a holder built from plywood. In this position, most of the smoke dispersed into the atmosphere resulting in very little green staining of snow near the discharged devices. At the time of the test, there was a light wind. The corresponding multiple increment snow samples for this activity are CEA4-3 #47-49 (Table 6). A final test involved discharging a smoke grenade over a tray and then collecting the particles in a sample jar (Figure 12).

Figure 10. Upright holder for M18 Green Signal Smoke Hand Grenade test.

Figure 11. Dispersion of smoke from five M18 Green Signal Smoke Hand Grenades during upright test.

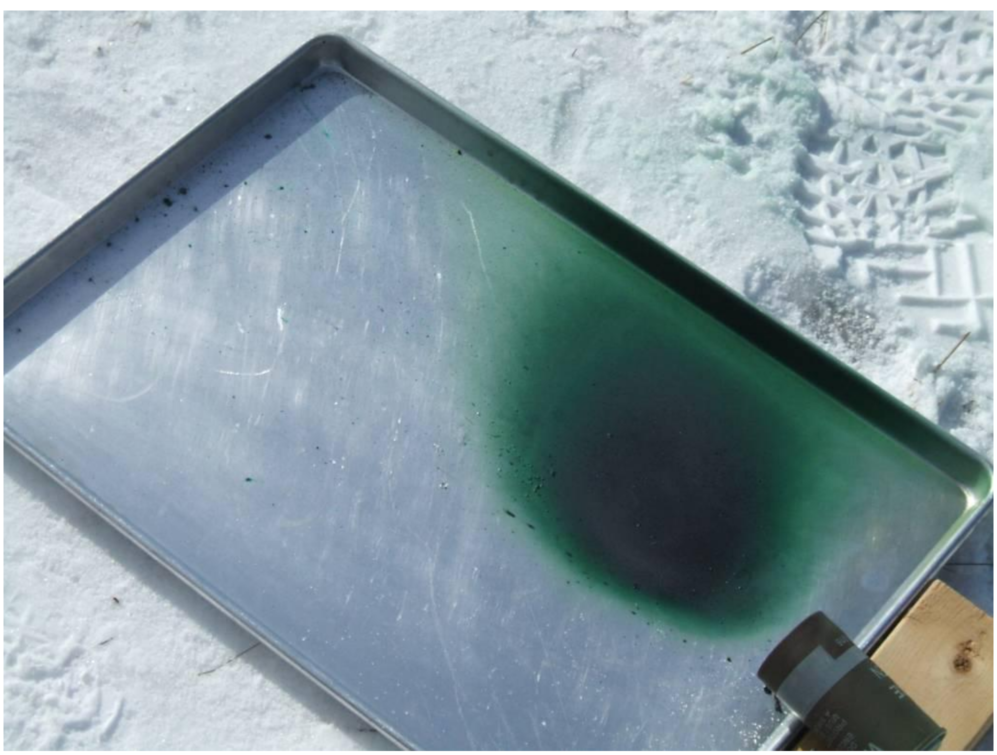

Figure 12. Residue from detonation of M18 Green Signal Smoke Hand Grenade.

3.1.2 M21 Flash Artillery Simulator

Ten of the M21 Flash Artillery Simulators were simultaneously triggered electronically on snow (Figure 13) by wiring five simulators in series and another five in series but parallel to the first set. Figure 14 shows the detonation was relatively small with most residues confined in the immediate area of the devices. However, it is clear that larger chunks of debris, mostly paper, are expelled beyond the smoke. The smoke dissipated in place with very little downwind transport. The residue produced from the detonation was confined to a relatively small area 3 x 3 m. Three multi-increment snow samples, CEA4-3 # 12-14, were collected (Table 6). Three aluminum trays were situated in a manner closest to the detonation, a middle downgradient location, and a further downgradient location (Figure 15). The residues were swept off each tray and the samples are designated CEA4-3 #15-17 (Table 6). Then each tray was rinsed with deionized water and the rinseate collected, e.g. sample identification CEA4-3 #20-22 (Table 6).

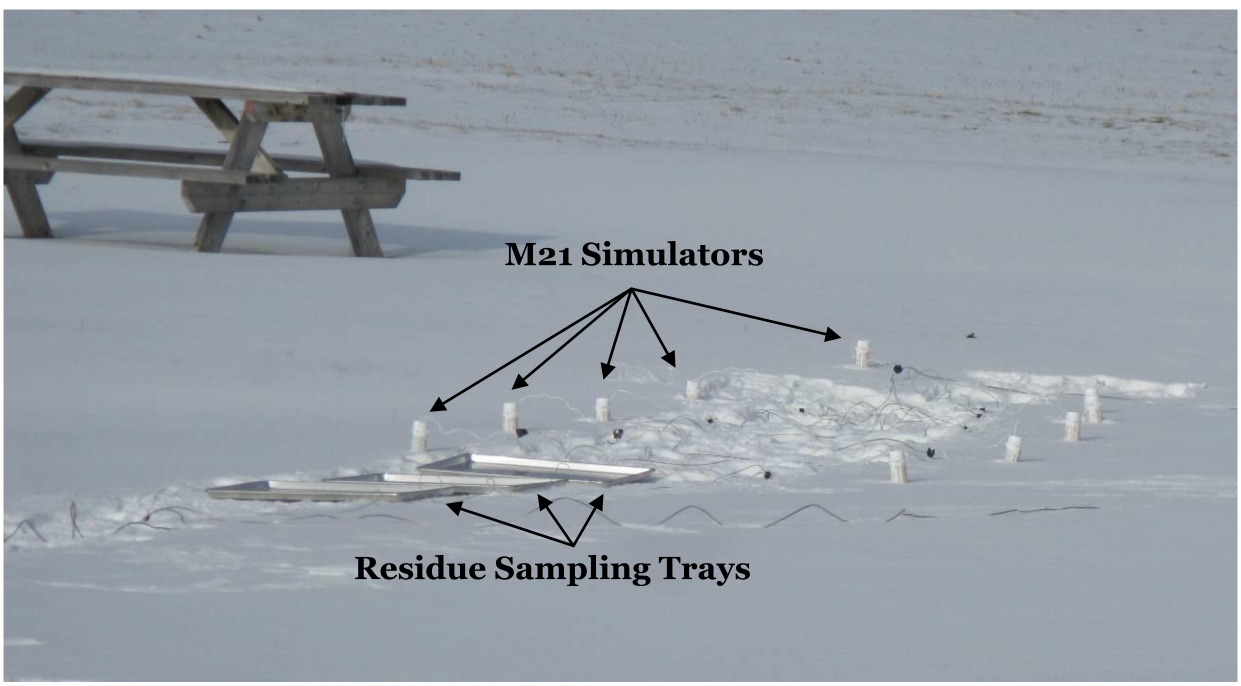

Figure 13. M21 Flash Artillery Simulator detonation layout, Test 1.

Figure 14. Simultaneous detonation of ten M21 Flash Artillery Simulators, Test 1.

Two additional simultaneous tests of ten M21 simulators were conducted (Figures 15 and 16) using the same setup as the first test. In both cases, the residue was easily visible on the snow surface and an area roughly 3 x 3 m was marked out for sampling. For both tests, multi-increment snow samples were collected from the residue-affected area or Decision Unit (DU). Approximately 50 increments were collected per DU. The sample identification numbers were CEA4-3 #51-53 for Test 2 and 55-57 for Test 3 (Table 6). As part of Test 2, an aluminum tray was set out and particulate residues collected (Figure 17).

Figure 15. Residue from ignition of ten M21 Flash Artillery Simulators, Test 2.

Figure 16. Residue from ignition of ten M21 Flash Artillery Simulators, Test 3.

Figure 17. Particulates collected from ignition of ten M21 Flash Artillery Simulators, Test 2.

3.1.3 M117 Booby Trap Flash Simulator

Ten of the M117 Flash Artillery Simulators were simultaneously initiated on snow for Test 1 using a wood holder (Figure 18) using a pull cord attached in series to the activation cord on the simulator with another five simulators connected in series but parallel to the first set of simulators. The distribution pattern of residue was similar to the M21 tests but covered a smaller 1 x 1 m area. Because the impacted area was smaller than the M21 tests the entire surface snow layer, < 2 cm, containing residue was recovered. The entirety of the residue affected area was collected as samples CEA4-3 #42, 43, 45 (Table 6). A second ignition of ten M117 simulators was also conducted in a clean area for replication of the first test with the entirety of the residue impacted snow surface collected, e.g. sample CEA4-3 #46-1, 46-2, 46-3 (Table 6).

Figure 19. Preparation of M117 Booby Trap Simulators for ignition.

3.1.4 M127A1 White Illumination Ground Parachute Signal

Testing of the M127A1 device occurred at Range 74. Because this device is air launched, the dispersion pattern from proper use of the M127A1 is very large—tens of acres making it unlikely that residue levels are detectable. The propellant for the M127A1 is black powder with all of the metals associated with the parachute candle. For these tests, therefore, the candle was removed and the propellant separately managed. A standing frame was constructed and the parachute hung on this device (Figure 19). The candle was ignited with a blow torch. Eight of the illumination devices were detonated per test. A slight wind was present during the tests (Figure 20). As shown by Figures 21 and 22, pieces of burning material fell to the ground beneath the flare. Following detonation, snow samples were collected beneath the device, immediately downwind of the device, and 10-m downwind (Table 6). In addition, tray samples were used to collect particulate residues (Figure 23).

Figure 19. Setup for M127A1 tests.

Figure 20. Dispersion of smoke during a M127A1 test.

Figure 21. Burning of a M127A1 flare.

Figure 22. Residue on snow from igniting a M127A1 flare.

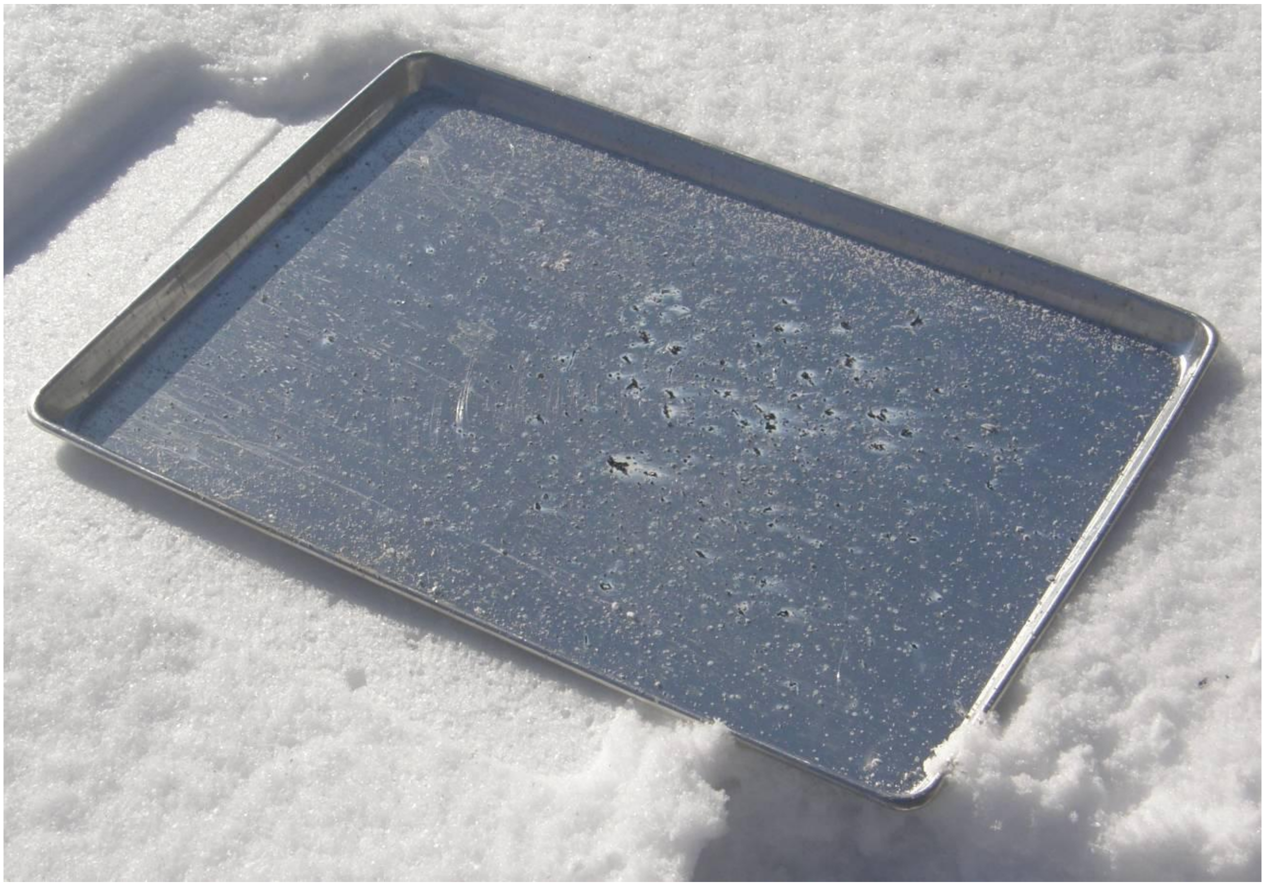

Figure 23. Residue collected on aluminum tray from igniting a M127A1 flare.

3.2 Field Sampling

3.2.1 Snow Sampling

Following each test, snow samples, either multi-increment or removal of the entire residue impacted area, were collected using the same techniques described by Walsh *et al.* (2007, 2005). Each multi-increment sample consisted of 50-increment snow samples collected from the depositional area. Typically, the area sampled included the detonation point and then an area downwind where residue was visible on the snow surface. In the case of the M18 green smoke grenade the snow was stained a green color. The M127A1 illumination device caused the deposition of black soot particles. The other two devices, M21 and M117, resulted in the deposition of black soot and paper. Sampling strategies included a spiral, systematic random and lap approach depending on the configuration of the residue plume. Samples were collected with a 10 x 10 cm stainless scoop to a maximum depth of 2 cm, and placed in clean polyethylene plastic bags, and labeled. When the entire residue impacted area was recovered, a stainless steel scoop was used to remove the top layer of snow (top 1 cm or less)

containing the residue. In the case of the green smoke grenades the green dye soaked into the snow and the entire area of green snow was removed. In most cases, this involved collecting snow to just above the soil surface.

Triplicate multi-increment background samples were also collected from the snow surface in an area near the entrance to Range 4-3, which was upwind of the pyrotechnic detonations. These samples had identification numbers of CEA4-3 #9-11 (Table 4). A multi-increment background snow sample was also collected from Range 74 prior to the M127A1 Signal Illumination Parachute Flare tests and is denoted as sample CEA4-3 #44 (Table 4). Once collected, the samples were returned to the Cold Regions Research and Engineering Laboratory (CRREL) Hanover, New Hampshire and stored in a dark cold room at a temperature of

-20^{o}C.

3.2.2 Tray Sampling

Sampling trays were used to collect metals for particle size analyses, X-ray analyses, and scanning electron microscopy (SEM). The trays serve a second function by providing a check on snow sample concentrations. In the event that the metal residue was hot enough to melt through the snow to depths below 2 cm, surface snow samples would miss this component but trays would collect the material.

Aluminum trays were placed on the snow near the detonation area for several tests (Table 4). In some cases the residue was easily swept off of the trays into sample jars. In other instances, it was not possible to sweep the dry residue off the tray because snow was deposited upon the trays and then quickly melted causing the soot particles to adhere to the trays. In such cases, the particles deposited on the trays were swept off using deionized water and the liquid placed in a 4-oz amber glass jar.

3.2.3 Rinseate Samples

Following the detonation tests, the spent M18 cartridge was recovered and the inside rinsed with 500 ml of deionized water. This sample was labeled CEA4-3 #25 (Table 4). The M21 and M117 devices left only limited paper debris after detonation so rinseate samples from the trays were not collected. The construction of the M127A1 device made it impossible to rinse. It should be noted that the US Army now has guidelines for the recovery and disposal of spent pyrotechnic devices. Previously, these devices were left on the range such that any residue could have been washed out by precipitation.

3.2.4 Soil Sampling

On June 30, 2010, soil samples were collected from the same areas as the proceeding winter pyrotechnic tests on snow (Table 7). All areas were sampled in triplicate using multi-increment sampling (Hewitt *et al.* 2009). A triplicate background soil sample was collected to correspond with snow samples CEA4-3, #9, 10, and 11 (Table 6). A 50-increment sample of the top 5 cm was obtained at evenly spaced locations throughout each area of interest. The CRREL Mult-Increment Sampling Tool (Walsh *et al.* 2009) was used to collect the samples, which typically weighed 0.5 kg. A total of 18 soil samples were collected.

Table 7. Soil sampling field information.

Sample ID	Range	Number Increments	Depth (cm)	Weight <2 mm (g)	Weight >2mm (g)	Replicate	Comments	Device
1	74	50	2.5	469.9	162.9	1	Corresponds to snow samples CEA4-3 # 33, 34, 35	M127A1 Para-chute Flare
2	74	50	2.5	552.1	143.7	2	Corresponds to snow samples CEA4-3 # 33, 34, 35	M127A1 Para-chute Flare
3	74	50	2.5	529.5	106.4	3	Corresponds to snow samples CEA4-3 # 33, 34, 35	M127A1 Para-chute Flare
4	74	50	2.5	492.1	246.8	1	Corresponds to snow samples CEA4-3 # 36, 37, 38	M127A1 Para-chute Flare
5	74	50	2.5	448.6	230.2	2	Corresponds to snow samples CEA4-3 # 36, 37, 38	M127A1 Para-chute Flare
6	74	50	2.5	391.6	182.5	3	Corresponds to snow samples CEA4-3 # 36, 37, 38	M127A1 Para-chute Flare
7	4-1	100	2.5	1207.5	136.3	1	Corresponds to snow samples CEA4-3 # 12, 13, 14	M21 Artillery Simulator
8	4-1	105	2.5	1182.2	123.4	2	Corresponds to snow samples CEA4-3 # 12, 13, 14	M21 Artillery Simulator
9	4-1	100	2.5	1141.7	142.5	3	Corresponds to snow samples CEA4-3 # 12, 13, 14	M21 Artillery Simulator
10	4-1	125	2.5	1552.3	78.9	1	Corresponds to snow samples CEA4-3 # 42, 43, 44	M117 Booby Trap Simulator
11	4-1	100	2.5	996.8	44.4	2	Corresponds to snow samples CEA4-3 # 42, 43, 44	M117 Booby Trap Simulator
12	4-1	100	2.5	874.8	62.8	3	Corresponds to snow samples CEA4-3 # 42, 43, 44	M117 Booby Trap Simulator
13	4-1	50	2.5	453.7	108.2	1	Corresponds to snow samples CEA4-3 # 9, 10, 11	Background
14	4-1	50	2.5	352.5	60.7	2	Corresponds to snow samples CEA4-3 # 9, 10, 11	Background
15	4-1	50	2.5	383.5	64.0	3	Corresponds to snow samples CEA4-3 # 9, 10, 11	Background
16	4-1	50	2.5	496.3	59.8	1	Corresponds to snow samples CEA4-3	M18 Smoke

Sample ID	Range	Number Increments	Depth (cm)	Weight <2 mm (g)	Weight >2mm (g)	Replicate	Comments	Device
							# 47, 48, 49	Grenade
17	4-1	50	2.5	604.9	108.7	2	Corresponds to snow samples CEA4-3 # 47, 48, 49	M18 Smoke Grenade
18	4-1	50	2.5	496.6	60.0	3	Corresponds to snow samples CEA4-3 # 47, 48, 49	M18 Smoke Grenade

3.3 Sample Preparation Methods

3.3.1 Water

Upon returning to the laboratory the snow samples were stored in a CRREL cold room at -20°C awaiting analysis. The bags were melted at ambient laboratory temperature overnight and then weighed to determine volume. Samples that had not completely melted were thawed with gentle agitation in a warm water bath. Each sample was vacuum-filtered through a Whatman glass microfiber grade GF/A 1.6 µm filter. Several filters were required per sample. These filters were reserved in individual plastic bags while the solid residue was split into two fractions. The aqueous sample was recovered and stored in polyethylene plastic bottles. One fraction of each snow sample and a selection of eluent from the filters were sent to EL (Environmental Laboratory, Vicksburg, MS) for analysis while the remaining samples were stored in the cold room at CRREL. All water samples were prepared for analysis at CRREL with a 100 mL portion of each snow sample acidified to 1% acid (v/v) using concentrated (70%) nitric acid (Fisher Scientific, Trace Metal Grade).

3.3.2 Filter Residue

After filtering of the snow was complete the residue and filter was dried and the sample weights recorded. Then, 0.5 g of residue was scraped off of the filter paper into a weigh dish for digestion. For filters containing less than 0.5 g, the entire solid residue was scraped into the digestion vial. For the filters with no visible residue, the filter was washed with 1 % HNO_3. The sample mass was calculated by measuring the dry weight of the filter before and after the wash.

Solid residue samples were digested in preparation for analysis following a modification to USEPA SW-846 Method 3050B at EL. Initially, 5 mL of 50:50 HNO_3 was added to each sample and cooked at 95°C for 30 minutes on a SCP DigiPrep digestion block. Four subsequent additions of concentrated HNO_3 were

added followed by 30 minutes at 95°C. Two hours of heating at 95°C followed the fourth addition of concentrated HNO_3. Samples then were allowed to cool to room temperature and 3 mL of 30% H_2O_2 was added followed by 15 more minutes at 95°C. After the samples cooled, another 2 mL of H_2O_2 was added and the samples were heated for 2 more hours. After cooling to room temperature, the samples were filtered through a Whatman Grade 41 20-µm filter and diluted to 50 mL.

After analysis at EL the filter digest solutions described above were shipped back to CRREL for confirmation (i.e. QA/QC testing). The 49 mL samples were diluted to 100mL using de-ionized water and split into two fractions. One fraction was analyzed at CRREL and the other retained for archival purposes.

The remaining filter solids were digested in their entirety following Method 3050B. Because of the large mass of material on some filters multiple individual digestions were performed. The digestate solution for a given filter was then combined and mixed. An aliquot was sent to APPL Laboratories, Clovis, CA for analysis and a split was retained for CRREL analysis.

3.3.3 Soil

Soil samples were transported to CRREL and air-dried on aluminum trays. Once air-dried each sample was passed through a #10, 2mm sieve. The weight of the < 2 mm and > 2 mm size fraction was recorded (Table 7). The < 2mm size fraction was ground using a Lab Tech Essa steel ring mill grinder (Model LM2, Belmont, Australia). The steel bowl and puck were cleaned after each grind by washing with soapy water, followed by an acetone rinse, and air-drying. Digestion of the soil samples generally followed USEPA Method 3050B. The one exception being that 2 g of soil was digested instead of the 0.5 to 1 g called for in the method to obtain a more representative sample. Subsampling to build the 2 g soil aliquot for digestion was performed using 20-increments.

3.4 Analytical Methods

Water samples were analyzed for metals at EL using a Perkin Elmer Sciex ELAN 6000 inductively-coupled plasma mass spectrometry (ICP-MS) instrument according to USEPA Method 6020. In addition, water samples were analyzed for perchlorate, chloride, chlorite, and chlorate using the USEPA Method 300 series for ion chromatography analyses

A split sample was analyzed at CRREL using a Thermo Fischer iCAP 6300 Duo view Inductively Coupled Plasma spectrometer equipped with a CETAC ASX-520 auto sampler per USEPA method 6010. The operating conditions were set as follows: RF power at torch, 1150W; auxiliary gas flow rate 0.5 L/min, nebulizer gas flow rate, 0.7 L/min and pump flow rate 50rpm.

3.5 Residue Characterization Methods

The pyrotechnic residues were imagined using an FEI XL-30 field SEM at Dartmouth College. The SEM had both secondary and backscatter electron (BSE) detectors and an X-ray microanalysis light element Si(Li) detector for analyses of all elements heavier than carbon. Each sample was sprinkled onto a sticky carbon surface placed on an aluminum Cambridge stub. The stubs were then carbon coated to provide a conducting surface and minimize electrical charging of the surface.

4 RESULTS

The results from each of the pyrotechnic tests are presented by device tested. When multiple tests of the same device were conducted, each is presented separately. The quantity of the metal in the melted snow samples was determined separately from the metal retained in the filters. The total mass collected from each detonation experiment, therefore, is the sum of the mass in solution (in the snow) and in the solid residue on the filters. Because, the material collected on the aluminum collection trays was used for surface analytical analysis the metal content was not quantified and therefore not included in the metal mass calculations. The total residue mass on the aluminum collection trays was a fraction of 1 percent of the total residue mass obtained in the snow samples. Thus, the absence of the residue collected on the aluminum trays in the metal mass calculations has little influence on the final results.

4.1 Composition of the residues

An SEM and energy dispersive X-ray (EDAX) system was used to image and analyze the pyrotechnic residues deposited onto the aluminum trays and from selected snow samples. These data allowed the size and shape of the metals to be determined and helped confirm the presence of constituent metals in the pyrotechnics.

4.1.1 Background snow sample

Material collected from the background snow samples were filtered (Figure 24) to determine what types of materials were naturally deposited on the snow cover. Particles smaller than 100μm in diameter, fibers, and plant material were found. The particles are likely soil grains as they contain silicon, oxygen, aluminum, calcium, and potassium, a composition consistent with quartz and feldspar mineral grains.

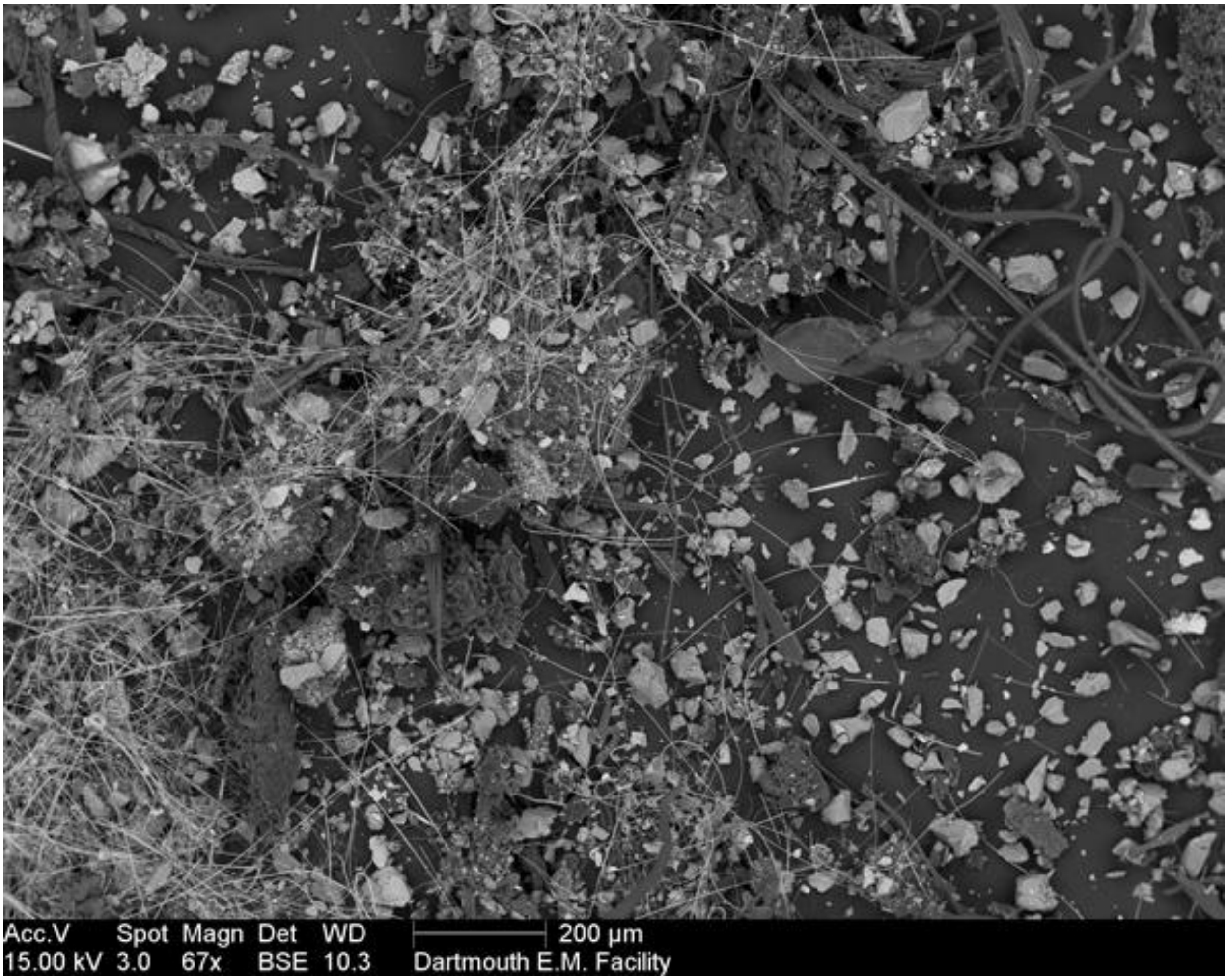

Figure 24. Backscatter electron image of particles found on filters used for the background sample.

4.1.2 M18 Smoke Hand Grenade

The M18 smoke hand grenade detonations (Figure 25a) deposited particles that are >200µm in size and are mainly carbon aggregates. The bright particles (Figure 25b,c) found on the tray surface were soil grains- quartz and feldspars. No metal was detected in the sample but a little potassium was found, probably from the potassium chlorate, one of the main constituents in the grenades. Magnesium carbonate is another main ingredient of the M18 smoke grenade but no magnesium was found.

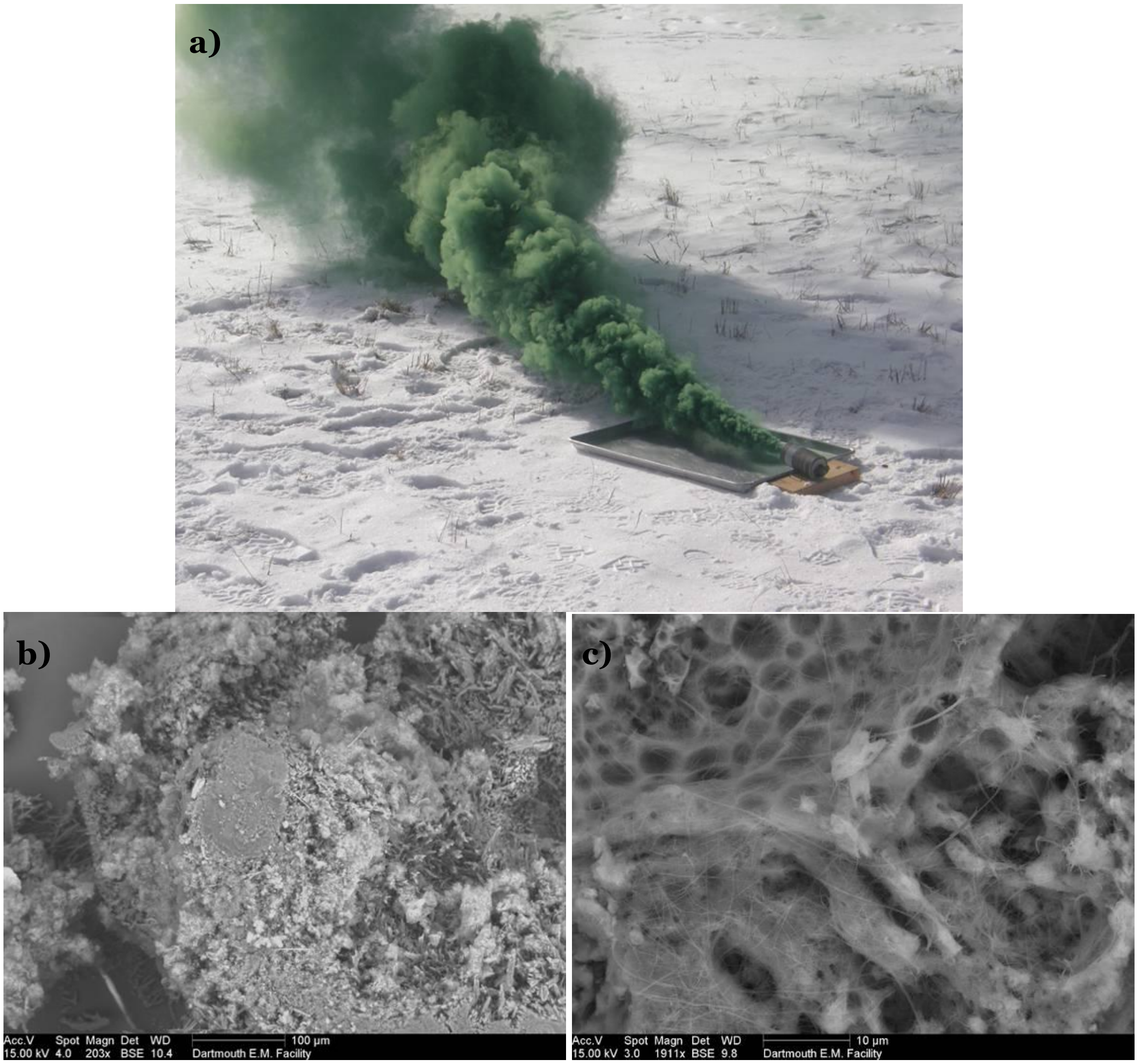

Figure 25. Residue deposited by the M18 Smoke Hand Grenade: a) residue cloud; b) low magnification backscattered electron image of residue; c) higher magnification image of carbon matrix.

4.1.3 M21 Artillery Flash Simulator

The artillery flash simulator detonation (Figure 26a) deposited small particles that were less than 50µm (Figure 26b). Most of the residue was carbon-rich and was embedded with aluminum oxide spherules and needle-shaped barium-rich particles (Figure 26c, d). The spheres contain aluminum, barium, sulfur, and oxygen and are 1 to 10µm in diameter. Very bright spherules also contained calcium. The needle-shaped grains were mainly barium and oxygen (Figure 26d) and were ~5µm in length. The two main primary metal constituents in the flash simulator are barium nitrate and aluminum powder.

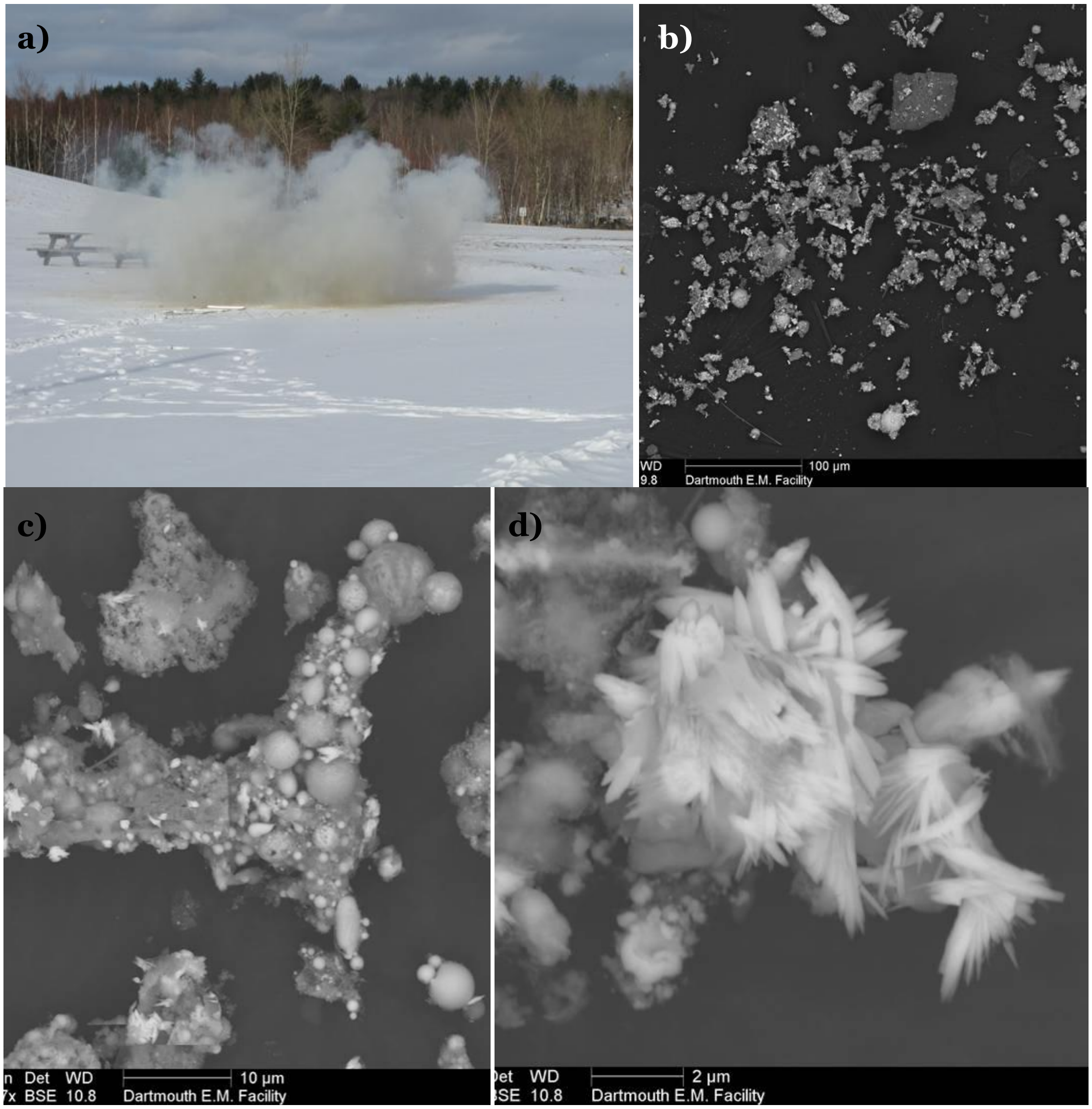

Figure 26. Residue deposited by the M21 Artillery Flash Simulator: a) residue cloud; b) low magnification backscattered electron image of residue; c) aluminum oxide spheres in a carbon matrix; d) needle-shaped barium-rich particles.

4.1.4 M117 Booby Trap Simulator

The primary metal constituents of the Booby trap simulator are antimony, magnesium, potassium, and phosphorous. Detonation (Figure 27a) of this device deposited 100 to 200µm-sized particles. Some of these were carbon with <20µm-sized metal grains attached (Figure 27b) others were metal spheres (Figure 27c). Bright spheres contained aluminum and oxygen; darker spheres were mostly magnesium and oxygen. Very bright particles contained antimony and sulfur (Figure 27c,d) consistent with the presence of antimony sulfide in the pyrotechnic

formulation. Some soil grains were also found and are probably feldspars as they contain silicon, aluminum, sodium, and potassium.

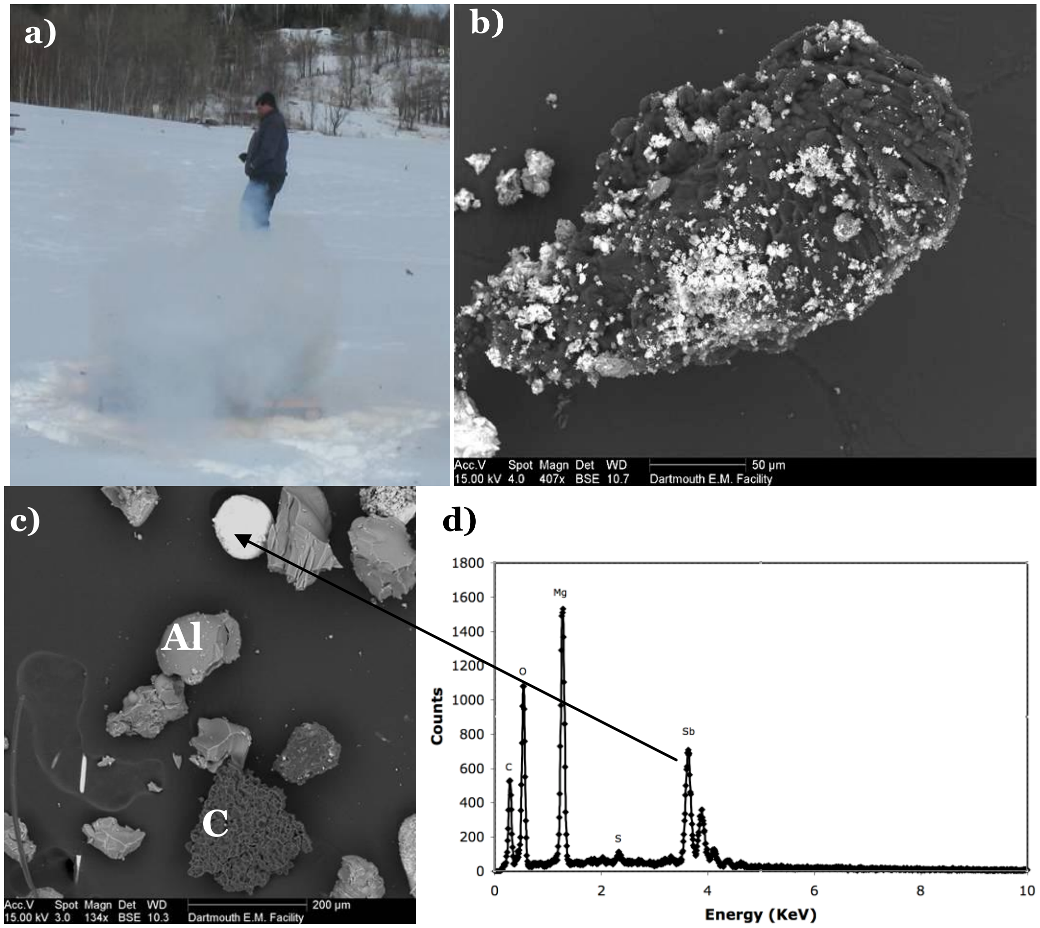

Figure 27. Residue deposited by a M117 Booby Trap Simulator: a) residue cloud; b) backscattered electron image of carbon grain with attached metals; c) image showing carbon grains, aluminum oxide sphere and antimony sphere; d) spectrum of antimony sphere.

4.1.5 M1271A Signal Illumination Ground White Star Parachute

The M1271A filter detonation residues (Figure 28a) contained mm-sized clumps that were often cracked and broken up into 200µm-sized pieces (Figure 28b). These clumps had areas containing sodium, oxygen, and magnesium (dark gray in Figure 28c) and areas that contained magnesium, oxygen, aluminum, silicon, and potassium. Small, 10µm, FeS beads were embedded in the clumps. Bright 1µm-sized grains on their surfaces contained barium and sulfur (Figure 28d,e). Residues deposited on one of the aluminum trays, directly below the device, contained a white powder that was predominantly sodium oxide (Na2O) with a small amount of magnesium and aluminum (Figure 28f,g). Burning of sodium in air will produce Na_2O. Carbon micro-tubes were also found. Magnesium and

sodium were the dominant residues, consistent with the composition of these flares which contain magnesium and sodium nitrate. The flares also contain potassium nitrate but potassium was not observed.

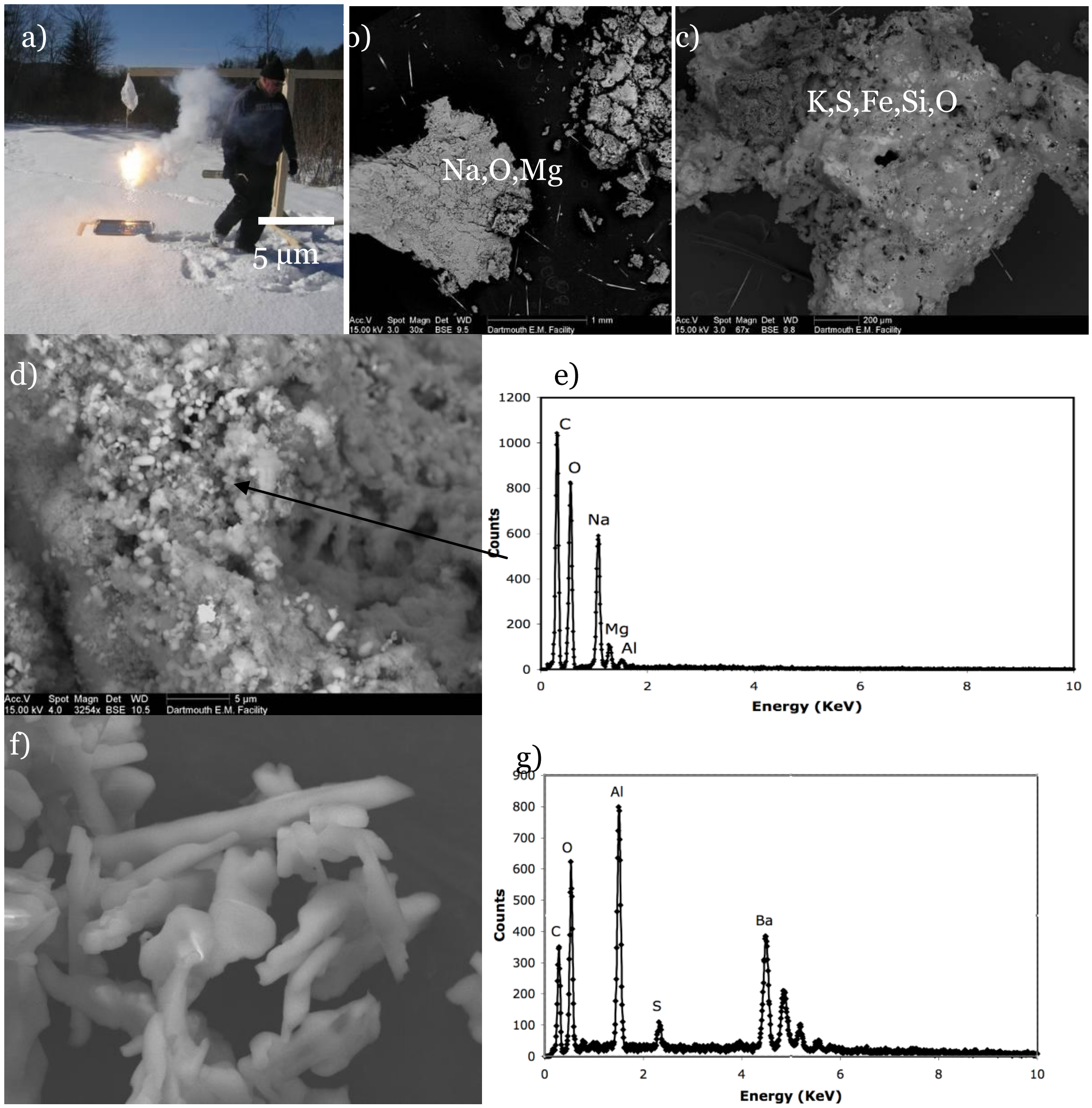

Figure 28. Residue deposited by the M1271A Signal Illumination Ground White Star Parachute: a) residue cloud; b) backscattered electron image showing sodium-rich (dark gray) and potassium-rich (light gray) regions; c); spectrum of barium-rich spot (white); f) sodium oxide residue; g) spectrum of residue shown in (f).

4.2 Metal Recovery

This section discusses the metals detected in the melted snow samples as well as the metal residue retained on the filter from melting the snow. The complete list

of solid residue results is in Appendix B and results for snow are found in Appendix C.

Snow and solid residue samples were analyzed at EL by ICP-MS and at CRREL using ICP-optical emission spectrograph (OES). The ICP-MS has a several order of magnitude lower reporting and detection limit than the ICP-OES. Consequently, the snow data from EL often had a reportable concentration for antimony, chromium, and zinc whereas the CRREL result was reported as not detectable. Although a lower detection limit was possible for cobalt and lead with the ICP-MS all the snow results were reported as below the detection limit. Except for the differences in detection limit there were no apparent significant differences in reportable concentrations for metal in snow. Therefore, the concentration data in Tables 8-20 and associated metal mass calculations are primarily derived from the CRREL generated snow data. However, in cases where the metal concentration was not detectable with the CRREL instrument, results from EL are used for the snow samples.

The precision of replicate snow samples was assessed for both the CRREL and EL datasets (Appendix D, Tables D-1 and D-2). Typically, a percent relative standard deviation (RSD) of 30 percent or less is targeted. However, many of the results were generally above this target. The standard multi-increment sampling methodology was followed for collection of the snow samples so the cause of the large sampling error is unclear. The same sampling approach was used for collection of the soil samples and the estimates of precision based on replicate sample collection and analysis was generally <30%. The concentration of metals in the snow is relatively small resulting in limited error in the corresponding amount of metal mass calculated.

During filtering of the snow samples a significant mass of residue was collected on the filter paper, often more than 100-g of material. Typically, digestion following USEPA Method 3050B suggests collection and digestion of 1-2 g of material. Two different approaches were used for this study to measure the concentration of metal in the snow filter residue. First, a 5-g subsample for digestion was obtained by subsampling using 20-increments. Then, after all of the study samples had been digested and analyzed in this manner the remaining filter residue was completely digested at APPL Laboratories and analyzed. A comparison of the metal mass calculations for partial digestion and analysis at CRREL and complete digestion and analysis by APPL Laboratories yielded little difference in results (Appendix D, Table D-8). Therefore, for the metal mass calculations discussed later in this section the results from CRREL were used.

A comparison was also made between the analytical results from CRREL and EL whereby both laboratories analyzed the same digestion solution for the filter residue samples. As noted earlier, the digestions were performed at EL with the samples initially analyzed at this location with ICP-MS. The digestate solution was then sent to CRREL and this solution was analyzed on June 1, 2010 and September 8, 2010. The CRREL analysis was performed approximately 1-month after the EL analysis and precipitates were noted to be present in the digestate solutions for some of the samples. However, the results between the two laboratories were not significantly different for most samples (Appendix D, Table D-5) so the CRREL filter residue results were used in all mass calculations

4.2.1 M18 Smoke Hand Grenade

Tables 8-10 show the concentration of metal collected in snow (dissolved and solid residue) from the various experiments with the M18 smoke grenade. The metal constituents known to be present in the grenades are; barium, iron, lead, manganese, magnesium, potassium, titanium, and zirconium. Titanium and zirconium were not analyzed in the snow samples because of the need for a different analytical method, the lack of regulatory screening values, and the very small mass in the grenade.

The smoke grenades were ignited in buried, horizontal-on-surface, and upright positions. The data demonstrate the significant effect of the orientation of the device when performing the experiment.

Each of the buried and horizontal experiments consisted of three replicate tests. Therefore, three metal snow concentration values are reported in Tables 8 and 9. For the buried smoke grenade test, two subsamples consisting of 20-increments were collected from the solid residues with the results reported in Table 8. For the horizontal smoke grenade test, a single subsample of the solid residue was collected and analyzed. For the buried and horizontal experiments, the entirety of green-stained snow was collected.

In the upright detonation experiment a single test was conducted but with 16 grenades. Triplicate multi-increment samples were collected from the visibly-stained snow surface. Thus, three metal results are reported for the snow samples in this test (Table 10). A single subsample was collected from the solid residue and analyzed.

In Tables 8-10 the amount of iron and manganese measured in the dissolved portion of the snow sample was below the quantitation limit for the ICP-OES at CRREL. Therefore, the data reported in the table are the ICP-MS results from EL.

The concentration of metal in the snow sample from the different field tests of buried and horizontal smoked grenades (Tables 8 and 9) and replicate samples for the upright tests indicate similar values with reported concentrations within a factor of two or better.

Table 8. Metal concentration in replicate snow and duplicate filter residue samples from M18 Smoke Grenade buried in snow.

Metal	Number of Rounds per Test	Affected Area (m2)2	Affected Area Sampled (%)3	Test Snow Concentration (mg/L)[4]	Background Snow Concentration (mg/L)[4]	Solid Residue Concentration (mg/kg)[4]	Background Solid Residue Concentration (mg/kg)
Barium	3	NA	100	0.42 0.28 0.12	0.04[1] 0.02[1] 0.02[1]	220 51.5	22.0
Iron	3	NA	100	0.01 0.005 0.007	0.01 0.02 0.02	3000 190	800
Lead	3	NA	100	0.0006[1] 0.0005[1] 0.0006[1]	0.0005[1] ND[1] ND[1]	83.2 0.6	1.34[1] 33.6[1]
Magnesium	3	NA	100	57.7 82.7 44.3	0.09 0.09 0.10	1,200 166	275
Manganese	3	NA	100	0.06[1] 0.08[1] 0.05[1]	0.01[1] 0.01[1] 0.009[1]	210 2.1	13.6[1] 313[1]
Potassium	3	NA	100	20.0 18.5 14.5	ND ND ND	830 89.7	93.4

[1]CRREL did not detect lead or manganese in the test snow samples nor barium, lead, or manganese, in the background snow samples. EL had a lower detection limit hence, these values are from EL. EL did not analyze for potassium.

[2]The smoke grenades were buried and therefore a determination of the impacted area from particulate deposition is not appropriate.

[3] The entire volume of visibly stained snow was removed.

[4]Multiple results represent analysis of field replicate/duplicate samples.

Table 9. Metal concentration in snow and solid residue samples from M18 Smoke Grenade lying horizontally on the snow surface.

Metal	Number of Rounds per Test	Affected Area (m^2)	Affected Area Sampled (%)[2]	Snow Concentration (mg/L)[3]	Background Snow Concentration (mg/L)[3]	Solid Residue Concentration (mg/kg)	Background Solid Residue Concentration (mg/kg)
Barium	3	<0.5	100	0.88 0.50 0.35	0.04[1] 0.02[1] 0.02[1]	4,100	22.0
Iron	3	<0.5	100	0.004 0.005 ND	0.01 0.02 0.02	1,700	800
Lead	3	<0.5	100	0.0005[1] <0.0004[1] <0.0004[1]	0.0005[1] ND[1] ND[1]	30.9	1.34[1] 33.6[1]
Magnesium	3	<0.5	100	8.63 9.22 5.90	0.09 0.09 0.10	12,800	275
Manganese	3	<0.5	100	0.006[1] 0.02[1] 0.007[1]	0.01[1] 0.01[1] 0.009[1]	41.5	13.6[1] 313[1]
Potassium	3	<0.5	100	51.4 30.1 25.1	ND ND ND	440	93.4

[1]CRREL did not detect lead or manganese in the test snow samples nor barium, lead, or manganese in the background snow samples. EL had a lower detection limit hence, these values are from EL. EL did not analyze for potassium.

[2]The entire volume of visibly stained snow was removed.

[3]Multiple results represent analysis of field replicate samples.

Table 10. Metal concentration in replicate snow and solid residue samples from M18 Smoke Grenade detonated in an upright position on the snow surface.

Metal	Number of Rounds per Test	Affected Area (m^2)[1]	Affected Area Sampled (%)	Snow Concentration (mg/L)[3]	Background Snow Concentration (mg/L)[3]	Solid Residue Concentration (mg/kg)	Background Solid Residue Concentration (mg/kg)
Barium	16	15	100	0.38 0.42 0.33	0.04[1] 0.02[1] 0.02[1]	11,000	22.0
Iron	16	15	100	0.02 0.003 0.002	0.01 0.02 0.02	820	800
Lead	16	15	100	<0.0004[2] 0.0004[2] <0.0004[2]	0.0005[1] ND[1] ND[1]	55	1.34[1] 33.6[1]
Magnesium	16	15	100	7.56 8.43 7.08	0.09 0.09 0.10	22,400	275
Manganese	16	15	100	0.006[2] 0.003[2] 0.004[2]	0.01[1] 0.01[1] 0.009[1]	100	13.6[1] 313[1]
Potassium	16	15	100	46.0 69.1 47.4	ND ND ND	680	93.4

[1]CRREL did not detect Pb or Mn in the test snow samples nor Ba, Pb, or Mn in the background snow samples. EL had a lower detection limit hence, these values are from EL. EL did not analyze for K.

[2]CRREL did not detect Pb or Mn. EL had a lower detection limit, hence, these values are from EL.

[3]Multiple results represent analysis of field replicate samples.

Tables 11-13 present the observed concentrations from Tables 8-10 in the form of a calculated metal mass. The metal mass was calculated using the following equation;

$$1\}\ T_{MM} = (M_K - ((S_C - S_B * V_s) + (F_C - F_B * M_{FR}))) / DT$$

where

T_{MM} = total metal mass (g),
M_K = known metal mass from MIDAS database (mg),
S_C = average metal snow concentration for test (mg/L),
S_B = average background metal snow Concentration (mg/L),
V_s = volume of melted snow (L),

F_C = metal filter residue concentration for test (mg/kg),
F_B = metal background filter residue concentration (mg/kg),
M_{FR} = total mass of filter residue (mg), and
DT = number of devices tested.

Even when buried, much of the metal was dispersed into the atmosphere, except for barium, because the heat from the grenade quickly melted the overlying snow (Tables 11 and 12). The majority of the metals had recoveries less than 2 percent with barium being the highest recovered metal at 86 percent. The high barium recovery may be a function of its high solubility and diffusion into the snow. Nonetheless, the buried grenade experiment captured at least ten times more metal per device than the experiment conducted with sixteen grenades upright above the snow (Table 13). Because M18s would ordinarily be tossed and end up on their side; the experiments demonstrate that the majority of the metal liberated during ignition is lost to the atmosphere or downwind.

Table 11. Metal deposition mass from M18 Smoke Grenade buried in snow.

Metal	Known Mass from MIDAS[3] (mg)	Snow Average Mass (mg) Tests 1 - 3[1]	Solid Residue Average Mass (mg)[1]	Mass Recovered per Device (mg)	Recovery (%)[4]
Barium	17.42	3.7	11.3	14.9	86
Iron	5.4	0.09	83.8	Undetermined[3]	Undetermined[3]
Lead	210.2	0.008	1.70	1.70	< 1
Magnesium	15,976	61	45.8	110	< 1
Manganese	252	0.81	4.40	5.20	2
Potassium	26,619	237	28.3	265	1
Titanium	20.8	NA	NA	NA	NA
Zirconium	19.5	NA	NA	NA	NA

[1]Buried refers to the position of the smoke grenade when detonation occurred: Buried=buried in snow. The values for "buried" are the average from a single grenade with the experiment conducted three times.

[2]Undetermined indicates more mass was measured in the background filter samples than on the test sample filters.

[3]MIDAS, 2009

[4]Values corrected with background metal levels.

NA – not analyzed

Table 12. Metal deposition from M18 Smoke Grenades residing horizontally on snow surface.

Metal	Known Mass from MIDAS[4] (mg)	Snow Average Mass (mg) Tests 4 - 6[1]	Solid Residue Average Mass (mg)	Mass Recovered per Device (mg)	Recovery (%)[5]
Barium	17.42	1.70	4.90	6.66	38
Iron	5.4	Undetermined[2]	2.00	2.01[3]	35[3]
Lead	210.2	0.0002	0.04	0.04	< 1
Magnesium	15,976	27	15.3	42.3	< 1
Manganese	252	0.009	0.05	0.06	< 1
Potassium	26,619	110	0.53	110	< 1
Titanium	20.8	NA	NA	NA	NA
Zirconium	19.5	NA	NA	NA	NA

[1]Surface refers to the position of the grenade when detonation occurred: Surface=residing on snow. The values for "surface" are the average from a single grenade with the experiment conducted three times.

[2]Undetermined indicates the metal concentration was below the quantitation limit.

[3]The calculated mass recovered and background corrected percent recovery per device was based on the average filter snow result from Tests 1-3, in Table 6.

[4]MIDAS, 2009

[5]Values corrected with background metal levels.

NA – not analyzed

Table 13. Metal deposition from M18 Smoke Grenade detonated upright in a holder.

Metal	Known Mass from MIDAS[4] (mg)	Snow Average Mass (mg) Upright[1,2]	Solid Residue Average Mass (mg) Upright[1,2]	Mass Recovered per Device (mg)	Recovery (%)[5]
Barium	17.42	0.38	4.4	0.30	1.7
Iron	5.4	Undetermined[3]	0.33	0.02	Undetermined[3]
Lead	210.2	0.00008	0.02	0.001	< 1
Magnesium	15,976	7.70	8.9	1.03	< 1
Manganese	252	Undetermined[3]	Undetermined[3]	Undetermined[3]	Undetermined[3]
Potassium	26,619	54.0	0.27	3.40	< 1
Titanium	20.8	NA	NA	NA	NA
Zirconium	19.5	NA	NA	NA	NA

[1]Upright refers to the position of the grenades when detonation occurred: Upright=detonated upright, above the snow, in holders. The "upright" value is the average of triplicate multi-increment samples.

[2]These results represent the total from 16 grenades.

[3]Undetermined indicates more mass was measured in the background filter samples than on the test sample filters.

[4]MIDAS, 2009

[5]Values corrected with background metal levels.

NA – not analyzed

Although, a solid residue mass of 83.8 mg was calculated for iron based on the concentration results in Table 8 the amount of iron measured in the solid residue sample from the background sample was even higher. If the measured iron mass from the test was subtracted from the background value a negative recovery would have been reported. Therefore, the mass of iron recovered was reported as undetermined.

In the case of Table 12, the iron result for the solid residue sample is listed as undetermined because the iron concentration in the background sample was higher than the test sample. As shown in Table 10 the iron concentration in the snow sample was very low near the quantitation limit in two of the samples and non-detectable in the third samples. Since the mass in the solid residue was so much greater than that dissolved in the snow, the iron mass recovered per device was calculated just using the solid residue data.

In Table 13, the mass of iron on snow was undeterminable because the background iron snow concentration was again higher than the test samples. Given, the small mass of iron calculated based on the solid residue concentration data and the low mass recovered per device the percent recovery is likely very low, less

than 1 percent. This same issue applies to manganese where the background levels for both the solid residue and snow samples were greater than the concentrations observed for the tests.

The following points can be observed from the data:

1. For the most realistic configuration (the experiment with the grenades lying on the surface), the percent recovered for most metals was less than 2% indicating that most of the metal released under normal usage is widely dispersed. Iron and barium levels may be elevated in the immediate discharge area of the device.
2. As with the water samples, the mass collected depended on the test configuration, which decreased by one-to-two orders of magnitude from buried-to-surface-to-upright.
3. A greater percentage of the recovered mass was on the filters, as compared to the solution, for the elements barium, iron, lead, and manganese. Magnesium and potassium, consistent with their typical presence in soluble salts, were found in higher mass in the water sample. Therefore, the more soluble metals will dissolve into the snow to a greater degree resulting in higher recoveries.

4.2.2 M21 Artillery Flash Simulator

Table 14 shows the metal collected (snow and solid residue) from detonations of the M21 Artillery Flash Simulator. Cerium requires a special analytical procedure, does not have a regulatory action level, and the amount of mass in the device very small, and thus this analyte was not analyzed as part of this experiment. Ten simulators were detonated at once in three separate experiments referred to as Test 1, Test 2, and Test 3.

The data from Table 14 were converted to mass to compare against the reported mass for each metal as shown in Table 15. The calculations performed followed Equation 1 with the exception that the snow and filter residue concentrations used were the average of the multiple tests as well as the average of each field replicate from each test. The measured metal mass in the snow samples, among the three tests, agrees within an order of magnitude. These samples were collected from the visibly impacted area using a multi-increment sampling approach.

Table 14. Metal concentrations on snow from M21 Artillery Flash Simulator detonations.

Metal	Number of Rounds per Test	Affected Area	Affected Area Sampled (%)[1]	Background Snow Concentration (mg/L)[3]	Snow Concentration (mg/L) Snow[3]			Filter Residue Concentration (mg/kg)	
					Test 1	Test 2	Test 3	Test 1	Test 2
Aluminum	10	3x3 m	100	0.02 0.02 0.02	0.08 8.8 0.63	34.3 1.37 27.0	24.2 18.9 13.9	141,000	110,000
Barium	10	3x3 m	100	0.04[2] 0.02[2] 0.02[2]	100 170 190	390 310 280	220 240 210	30,500	3,600
Copper	10	3x3 m	100	0.008[2] 0.008[2] 0.007[2]	ND ND ND	ND ND ND	ND ND 0.30[2]	9,700	9,700
Iron	10	3x3 m	100	0.01 0.02 0.02	0.002 0.003 ND	ND ND ND	0.001 ND ND	1,200	900
Lead	10	3x3 m	100	0.005[2] ND[2] ND[2]	ND ND ND	ND ND ND	ND ND ND	240	240
Potassium	10	3x3 m	100	ND ND ND	ND ND ND	0.12 0.18 18.0	0.09 0.25 0.24	57.1	46.5
Zinc	10	3x3 m	100	0.01[2] 0.01[2] 0.01[2]	ND ND ND	ND ND ND	3.15[2] 3.14[2] 2.18[2]	45.7	37.3

[1]The entire affected area was subjected to MI sampling.

[2]EL detected Cu and Zn in certain snow samples for which CRREL reported no-detection. Also, no detections were observed for Ba, Cu, Pb, and Zn in the background snow samples. The detectable EL values are used in these instances.

[3]Multiple results represent analysis of field replicate samples.

Table 13 also shows the amount of metal collected on the filters for two of the experiments – Tests 1 and 2. The quantity of metal collected on these is varied by approximately a factor of four or less. Material from Test 3 was used for SEM and x-ray diffraction (XRD) analysis.

In general, the recovery in this experiment was quite low. Even if the background values for potassium and zinc had been zero, the apparent recoveries would have only been approximately 6% and 2%, respectively. In summary, the following observations can be made:

1. Recovery for any particular metal did not exceed 0.5%.

2. More mass was collected on the filter for aluminum, copper, iron and lead. Consistent with their greater solubility, more potassium and zinc were collected in the soluble fraction.
3. The barium mass was greater in the dissolved fraction than the filter for Test 2, but the opposite occurred for Test 1.

Table 15. Metal mass deposition from M21 Artillery Flash Simulator.

Metal	Known Mass from MIDAS (mg)	Snow Average Mass for Test 1 (mg)[1]	Snow Average Mass for Test 2 (mg)[1]	Snow Average Mass for Test 3 (mg)[1]	Solid Residue Average Mass for Test 1 (mg)	Solid Residue Average Mass for Test 2 (mg)	Average mass per device (mg)[1]	Average Recovery (%)[3]
Al	9,563	0.50	2.34	5.28	238	440	36.7	< 1
Ba	13,876	22.0	81.0	64.6	51.8	14.4	59.2	< 1
Ce	2	NA	NA	NA	NA	NA	NA	NA
Cu	1,055	ND	ND	0.02	16.4	38.9	2.8	< 1
Fe	53	ND	ND	ND	ND	1.18	0.28	< 1
Pb	15	ND	ND	ND	0.41	0.96	0.07	< 1
K	0.72	ND	0.04	0.06	ND	ND	0.05	Und[2]
Zn	31	0.43	0.66	0.79	ND	ND	0.64	Und[2]

[1]The numbers are the average of three replicate samples collected from a single test in which ten simulators were detonated. The mass provided is the calculated value for a single device.
[2]Und indicates "undetermined," that more mass was measured in the background snow samples than on the test snow samples.
[3]Values corrected using background results
NA – not analyzed, ND = not detected.

4.2.3 M117 Booby Trap Flash Simulator

The concentration of metal in snow and solid residue from the M117 Booby Trap Simulator test is presented in Table 16. Replicate analyses of the snow samples were generally consistent. The test result snow concentrations were substantially greater than the background snow values. Solid residue concentrations from the test were also significantly higher than the background solid residue concentrations.

Table 17 shows the metal mass deposited from detonations of the M117 Booby Trap Flash Simulator. Ten simulators were detonated at once in two separate experiments. The visibly impacted area was outlined and the entire snow surface, to 1-cm in depth, was removed. Hence, the third and fourth columns of Table 17 are the average of replicate samples where the entire area of residue was collected. The measured soluble metal is within a factor of approximately one and

a half between experiments. The deposited mass of metal recovered was generally higher than the previous two pyrotechnic devices discussed.

Table 16. Metal concentration of snow and solid residue samples from M117 Booby Trap Simulator tests.

Metal	Number of Rounds per Test	Affected Area	Area Sampled (%)	Snow[1] Concentration Test 1 (mg/L)	Snow[1] Concentration Test 2 (mg/L)	Background Snow Concentration (mg/L)	Solid Residue Concentration (mg/kg)	Solid Residue Background Concentration (mg/kg)
Antimony	10	1x1 m	100	39.0 33.4 43.8	32.2 59.2 49.6	ND[2] ND[2] ND[2]	370	0.16[2] 2.87[2]
Magnesium	10	1x1 m	100	38.3 31.1 28.4	36.9 36.4 28.5	0.09 0.09 0.10	71,700	275
Potassium	10	1x1 m	100	230 170 410	210 41.4 390	ND ND ND	760	93.4

[1]Three bags of snow were collected for each ten-device experiment.

Table 17. Metal deposition from the M117 Booby Trap Simulator.

Metal	Known Mass from MIDAS[4] (mg)	Solid Residue Mass Test 1 (mg)[1,3]	Solid Residue Mass Test 2 (mg)[2,3]	Solid Residue Maximum Percent Recovered	Solid Residue Average Mass per device (mg)	Average Measured Mass per Device (mg)	Percent Recovered[5]
Antimony	1,053	40	30	4	18.4	53.3	5
Magnesium	425	42	31	10	640	670	158
Potassium	864	279	178	32	6.67	240	27

[1]Samples were collected in three bags and labeled 42, 43, and 45 respectively.
[2]Samples were collected in three bags, combined and labeled sample 46.
[3]The Mass in Filtered Snow was determined from ten M117 Booby Trap Flash Simulators detonated above the snow in a wooden holder.
[4]MIDAS, 2009
[5]Value corrected using background mass.

Interpretation of these data is marred by the anomalous recovery for magnesium. Background results were low, but the quantity collected on the filter was much higher than the amount supposedly present in the device. The high concentration of magnesium was beyond the calibration range of the instrument. As with previous experiments, the potassium recovery was relatively high and most was found in the soluble fraction. In contrast, more antimony and magnesium were found on the filter.

4.2.4 M1271A Signal Illumination Ground White Star Parachute

Detonation of the M127A1 signal illumination ground white star parachutes was conducted on a test stand with the device suspended 2-m above the ground surface. Except beneath the test device, particulate residues were not visible on the snow surface. Despite the complexity of the sampling, the residue collected in snow was generally within a factor of two or less between the two tests. Sodium and lead were exceptions, differing by a factor of approximately five.

The highest concentrations of metals (aluminum, barium, chromium, potassium, sodium, and zinc) in the snow samples were those collected immediately beneath the flare (Table 18). Surprisingly, magnesium levels were higher in the samples collected 10 m downwind from the tests. The levels of metals at 10 m downwind were still above background levels

Tables 19 and 20 present the metal mass collected from the two separate tests. Notable exceptions are aluminum and iron for which very high results were obtained for the test 2 filter (sample 33). These results were outside the calibration range of the instrument and thus the values are considered unreliable with the mass loading values over estimated. In addition, the antimony measured in the background filter samples exceeded that from the sample filters making the apparent recovery negative.

These data demonstrate that the deposition rate of metal from the M127A1 device is low indicating that metal loss from the devices during detonation is widely dispersed into the atmosphere.

In summary, each of these devices is designed for maximum dispersal either to obscure vision or to provide a signal. The generally low metal recoveries demonstrate the wide dispersal.

4.3 Soil Samples

Multi-increment soil samples were collected at the locations where the tests were conducted. Summary data from the metals are presented in Table 21 with complete results provided in Appendix E.

Table 18. Metal concentration of snow and solid residue samples from M127A1 Signal Illumination Ground White Star Parachute tests.

Usage	Number of Rounds/ Test	Affected Area	Affected Area Sampled (%)	Test 1 Concentration (mg/L) in Snow Beneath Flare[1]	Test 2 Concentration (mg/L) in Snow Beneath Flare[1]	Test 1 Concentration (mg/L) in Snow 10 m Downgradient[1]	Test 2 Concentration (mg/L) in Snow 10 m Downgradient[1]	Background Snow Concentration[1] (mg/L)
Aluminum	8	10x10 m	20	0.005 0.02 0.006	0.07 1.57 0.005	0.09 0.04 0.02	0.01 0.01 0.02	0.02 0.02 0.02
Antimony	8	10x10 m	20	0.006 ND ND	ND 0.002 ND	ND[2] 0.0006[2] ND[2]	0.002 0.001 ND	ND[2] ND[2] ND[2]
Barium	8	10x10 m	20	0.52 2.02 0.60	1.51 3.02 1.26	0.07 0.01 ND	0.07[2] 0.02[2] 0.02[2]	0.04[2] 0.02[2] 0.02[2]
Chromium	8	10x10 m	20	0.004[2] 0.02[2] 0.006[2]	0.006[2] 0.003[2] ND[2]	ND[2] ND[2] ND[2]	ND[2] ND[2] ND[2]	ND[2] ND[2] ND[2]
Cobalt	8	10x10 m	20	ND[2] ND[2] ND[2]	ND[2] 0.0004[2] ND[2]	ND[2] ND[2] ND[2]	ND[2] ND[2] ND[2]	ND[2] ND[2] ND[2]
Iron	8	10x10 m	20	ND 0.001 0.02	ND ND ND	0.005 ND ND	0.005 0.006 ND	0.01 0.02 0.02
Lead	8	10x10 m	20	ND[2] 0.003[2] ND[2]	0.0006[2] 0.003[2] ND[2]	ND[2] ND[2] ND[2]	ND[2] ND[2] ND[2]	0.005[2] ND[2] ND[2]
Magnesium	8	10x10 m	20	0.15 0.02 1.58	0.02 0.009 0.14	2.92 3.68 1.79	2.50 1.44 2.09	0.09 0.09 0.10
Molybdenum	8	10x10 m	20	ND[2] 0.0005[2] ND[2]	ND[2] 0.0008[2] ND[2]	ND[2] ND[2] ND[2]	0.002[2] 0.003[2] 0.002[2]	ND[2] ND[2] ND[2]
Potassium	8	10x10 m	20	5.62 19.8 7.88	12.4 31.8 9.71	0.06 0.04 0.006	0.21 0.10 0.07	ND ND ND
Sodium	8	10x10 m	20	650 2100 670	800 1700 700	1.40 1.41 0.94	2.33 1.64 1.90	1.00 1.01 0.58
Zinc	8	10x10 m	20	0.003[2] 0.01[2] 0.002[2]	0.01[2] 0.01[2] 0.006[2]	0.004[2] 0.004[2] 0.003[2]	0.002[2] 0.003[2] 0.002[2]	0.01[2] 0.01[2] 0.01[2]

[1]Each test consisted of three detonations of eight flares followed by snow collection, triplicate multi-increment samples, immediately downwind and 10m downwind after each firing. Snow underneath the test area from the firing of all three tests was collected following all three detonations was collected and is also included.
[2]These analytes were not detected by CRREL and the reported results are from EL.

Table 19. Metal solid residue mass deposition from M127A1, Test 1.

Metal	Known Mass from MIDAS (mg)	Snow Average Mass (mg)[1]	Average Solid Residue Mass(mg) Beneath Test Stand	Average Solid Residue Mass (mg) 10m Downwind	Average Measured Mass per Device (mg)	Percent Recovered(%)[3]
Aluminum	4	0.03	25.7	0.76	3.33	92
Antimony[2]	6	ND	0.001	0.0007	0.0003	<1
Barium	217	0.63	0.62	0.87	0.82	< 1
Chromium	76	0.005	0.005	0.001	0.006	< 1
Cobalt	11	ND	0.01	ND	0.002	< 1
Iron	25	-	5.43	0.75	0.77	3
Lead	11	0.0005	0.02	0.0007	0.003	< 1
Magnesium	54,987	0.36	1,600	10.1	210	< 1
Molybdenum	15	0.0001	ND	ND	0.0001	< 1
Potassium	10,679	7.00	8,500	0.6	8.15	< 1
Sodium	6,669	540	5.50	1.53	540	8
Tungsten	182	NA	NA	NA	NA	NA
Zinc	842	0.0008	0.07	0.86	0.12	< 1

[1]Each test consisted of three detonations of eight flares followed by snow collection, triplicate multi-increment samples, immediately downwind and 10m downwind after each firing. Snow underneath the test area from the firing of all three tests was collected following all three detonations was collected and is also included.
[2]EL reported traces of antimony in a few samples. However, based on the QA review (Appendix E), the EL data were not used. Additionally, sample calculations with the EL results indicated percent recoveries <0.005.
[3]Values corrected for background metal mass. NA – not analyzed, ND – not detected

Table 20. Metal solid residue mass deposition from M127A1, Test 2.

Metal	Known Mass from MIDAS (mg)	Snow Average Mass (mg)[1]	Solid Residue Average Mass (mg)	Average Mass per Device (mg)	Percent Recovered[3]
Aluminum	4	0.04	61.4	7.70	212
Antimony[2]	6	ND	0.003	0.0004	< 1
Barium	217	0.85	1.67	1.06	< 1
Chromium	76	0.005	0.009	0.006	< 1
Cobalt	11	0.0001	0.02	0.003	< 1
Iron	25	ND	1300	160	645
Lead	11	0.00009	0.05	0.006	< 1
Magnesium	54,987	0.24	2,400	310	< 1
Molybdenum	15	0.0001	0	0.0001	< 1
Potassium	10,679	7.00	25.4	10.3	< 1
Sodium	6,669	120	11.8	120	2
Tungsten	182	NA	NA	NA	NA
Zinc	842	0.002	0.02	0.004	< 1

[1]Each test consisted of three detonations of eight flares followed by snow collection, triplicate multi-increment samples, immediately downwind and 10m downwind after each firing. Snow underneath the test area from the firing of all three tests was collected following all three detonations was collected and is also included.
[2]EL reported traces of antimony in a few samples. However, based on the QA review (Appendix E), the EL data were not used. Additionally, sample calculations with the EL results indicated percent recoveries <0.005.
[3]Values corrected for background metal mass.
NA – not analyzed, ND – not detected

Table 21. Comparison of averages of three background soil samples to fifteen soil samples collected underneath test locations.

Element	Al mg/kg	Ba mg/kg	Cr mg/kg	Cu mg/kg	Fe mg/kg	K mg/kg	Mg mg/kg	Mn mg/kg	Na mg/kg	Pb mg/kg	Sb mg/kg	Zn mg/kg
Test Mean	9,500	42	280	12	20,300	1,600	3,000	280	190	25	3.6	38
Background Mean	11,300	48	370	16	21,300	1,600	2,900	310	190	38	4.7	42

The average metal concentrations in three background soil samples are slightly higher as compared to the soil concentrations where the tests were conducted. All results, except chromium, are similar to soil and crustal averages (Table 4). Chromium values in the soils are high relative to the crustal values, but below the background levels. Adequacy of the background locations was demonstrated by comparing elements not found in the pyrotechnic devices. Of 22 elements analyzed, four were not detected at sample or background locations. Thirteen other elements were actually higher, on average, in the background samples than at the test locations. Of the remaining five elements, the sample locations had no more than a 6% greater percent difference.

5 DISCUSSION

5.1 M18 Green Smoke Grenade

The highest mass of metal observed in the snow and snow solid residue samples from the M18 smoke grenades was potassium followed by magnesium however, this represented less than one percent of the total mass of material in the device (Tables 11-13). The potassium originated from the potassium chlorate, potassium nitrate, and potassium perchlorate used in the formulation. Neither chlorate nor perchlorate was detected in the snow and snow solid residue samples from testing of the M18 green smoke grenade, although a significant quantity of potassium chlorate and potassium perchlorate is used in the filler for the device.

The highest percentage of recovered metal compared to the known formulation was barium with the recovery levels declining from the buried to horizontal discharge to upright discharge (86% to 38%, to 1.7%, respectively). The observed mass of barium in the snow and snow solid residue samples was very small consistent with the small quantities used in the formulation (Table 2). Whether the device was lying on its side or in a vertical position controlled the degree of deposition. When discharged in a horizontal position a green stain of several meters in length was visible on the snow surface. A green smoke cloud was dispersed into the atmosphere and visible 10's meters from the discharge point. Smoke grenades discharged vertically contributed to minimal staining of the snow surface in the vicinity of the smoke grenade. The green smoke dispersed and was visible to greater distance than horizontal tests. As will be discussed in Section 5.5 the amount of barium, mass, introduced into the environment is small. Any appreciable measurable buildup in the soil would require many devices to be used in the same location with little air dispersion.

Low chlorate levels were observed in the snow samples associated with the use of the green smoke grenade, which is consistent with its formulation. However, there are no regulatory action levels for chlorate. It is also possible for chlorate to be transformed to chlorite but no evidence of chlorite was found in the snow samples.

5.2 M21 Flash Artillery Simulator

Aluminum and barium yielded the largest mass of metal residue per device for the M21 flash artillery simulator (Tables 2 and 15). However, the mass per device and the recoveries were low. Less than one percent of the mass of material in the device was recovered. Detonation of these devices resulted in a white cloud of smoke which was quickly dispersed even under low wind conditions. Paper and residues were generally found within a 5-m radius of the detonation.

5.3 M117 Booby Trap Flash Simulator

The highest mass of metal residue observed with the M117 detonation were the metals magnesium and potassium with the highest recoveries as compared to the device formulation being magnesium, potassium, and antimony (Tables 2 and 17). A greater concern is the level of perchlorate detected in the snow samples from the test with the M117 Booby Trap Flash Simulator. Soil samples were not analyzed for perchlorate because it typically is not adsorbed by the soil. Snow concentrations of 100's mg/L were observed (Appendix C) suggesting concentrated use of a large number of the M117 device could result in groundwater impacts. Further studies would need to be conducted to assess whether perchlorate is really an issue.

5.4 M127A1 Signal Illumination Parachute

The largest mass of metal residue was associated with aluminum, sodium, potassium, magnesium, iron and aluminum (Tables 2 and 19). Recall that for this test, the propellant was separated from the device and the illumination round was ignited suspended 1-m above the ground surface. Normal operation of this device results in the illumination component being launched up to an altitude of approximately 100-m, with the illumination candle suspended by a parachute and carried by the wind. The one device launched in normal fashion was carried several hundred meters by low-wind conditions before the candle burned out. Although, snow samples were not collected it is likely that metal levels above background levels could not be discerned under such a test.

5.5 Metal Recoveries

Comparing the mass of metal recovered in the snow to the mass of metal present in the native soil provides an indication of whether the anthropgenically introduced metal could pose a risk. For example, the mass of lead collected from a buried M18 hand grenade was 1.7 mg (Table 9) as compared to a total of 0.001 mg (Table 11) collected from 16 of these grenades detonated in a more realistic

upright position. If it is assumed that the resulting lead residue from the buried grenade is deposited over a 1 x 1 m square area and infiltrates into the top 2 cm of soil and the average bulk density of soil equals 1.8 g/cm^3 then the soil mass in this volume of soil is 36 kg. Therefore, the concentration of lead in soil from detonation of one M18 smoke grenade is below 0.047 mg/kg and well below the USEPA PRG of 40 mg/kg. In addition, it bears repeating that this detonation scenario is unrealistic. Using the value from 16 grenades, detonated in the same location in an upright position, the calculated residue deposition is even less. The only way for the USEPA PRG value to be exceeded is if hundreds of detonations occurred in a fixed location and the deposited residue was limited to a confined area. It is emphasized, however, that these pyrotechnic devices are not used in this manner. During training the devices are randomly used over a large area and in conditions where wind would disperse the smoke residue. A similar calculation can be performed for barium, which had the highest recovery from the M18 device. In this case, using the buried test mass of 5.1 mg, the resulting increase in soil concentration is 0.14 mg/kg—again a value that would not be detected with standard sampling and analysis procedures.

A review of all of the metal data for each pyrotechnic device demonstrates that the only element which might be found in appreciable quantities is antimony from the M117. For the M117 device, the same calculation as above can be performed assuming an antimony residue mass of 53.3 mg. In this case, the soil concentration could increase by 1.5 mg/kg—an amount that should be detectable by normal field sampling and analysis programs. This level of antimony would exceed the USEPA PRG if more than two devices were detonated. The only other device with antimony, M127A1, did not contain enough of the metal to be measurable. However, as discussed in Section 3, antimony recoveries are poor with existing analytical techniques leading to uncertainty in the antimony results.

These results suggest that buildup of metals in soil from training with pyrotechnics by military personnel is likely not a significant issue for the MMRP. In particular, air launched devices are likely to have any metal residues dispersed into the atmosphere with fallout over a large area. Conventional soil sampling is not likely able to detect the metals and be able to differentiate between natural background levels. Even for ground detonated devices the metal buildup in the soil is not likely to be discernable above the background levels. Although, elevated metals were observed in the snow samples above background conditions the mass loading was quite low with the total mass for most analytes less than 1 percent of the total known mass in the device.

6 Conclusions

Four representative pyrotechnic devices (M18 Green Smoke Hand Grenade, M21 Flash Artillery Simulator, M117 Booby Trap Flash Simulator, and M127A1 Signal Illumination Parachute) were tested on snow to determine the mass loading rate of metal. The concentration of metal contributed per device to the environment was quite low and the metal recoveries as compared to the initial filler mass were also quite low. If soil sampling is relied upon to evaluate whether metals have been introduced to the environment from the use of a pyrotechnic device it is not likely that the levels observed could be discerned from the native background concentrations of metals in the soil. Therefore, sampling for metals from military pyrotechnic training does not seem warranted.

Although the focus of this document is on the metals present in the pyrotechnic compositions similar consideration should be given to perchlorate. A large number of pyrotechnic devices contain perchlorate salts, although perchlorate is an oxidizer and would be largely consumed in the reaction producing chloride. However, it should be recognized that any uncombusted salts would be rapidly dissolved, highly soluble, and recalcitrant. As a consequence, soil sampling would not provide an indication of perchlorates use and potential environmental impact because it would no longer reside in the soil column. Although, the MMRP is primarily focused on soil sampling to determine an environmental impact it is possible that perchlorate poses an environmental risk to groundwater. If perchlorate is a concern the only way to ascertain its presence will be through groundwater sampling because it is rapidly dissolved when in solid form on soil and transported away from the source area.

7 Recommendations

The amount of metal introduced into the environment from pyrotechnic training is very low and in most cases indistinguishable from background levels. Therefore, sampling for metals as a result of pyrotechnic training at MMRP sites is generally not recommended. However, if it is known that pyrotechnic training occurred in a specific fixed area over an extended period of time, then it is possible that metal levels in the soil could be elevated above background. This situation seems plausible only for ground-based devices.

In addition, where a pyrotechnic device underwent a low-order detonation or was a dud a sizable mass of metal would remain in the device and possibly on the soil and around the low-order. If the pyrotechnic was removed the probability of encountering the location of elevated metal soil concentrations is remote. In the past the low-order and duds may not have been removed from the training range. If these still exist, soil sampling could be targeted around the remaining device. A generic sampling design is presented in Appendix F.However, it should be kept in mind the soil area affected by a low-order or dud would be quite small and not likely represent a concern from a regulatory perspective.

For air-launched devices the degree of airborne dispersion of particulates is large enough that metal accumulation above background levels is extremely unlikely. If sampling is desired, the following is the proposed sampling plan to be used for assessing metals concentrations in surface soils at MMRP sites.

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APPENDIX A: SUMMARY OF PYROTECHNIC USAGE

Table A-1. Pyrotechnic munition usage at all Alaska Ranges from 1 August 2005 through 26 September 2008.

DODIC Number	Military ID	Military Name	Quantity Used	Number of Duds	Dud Rate (%)
Air Launched Illumination Munitions					
C449	M314	CTG 105mm Illumination	277		
B627	M83A1	CTG 60 mm Illumination	271	2	0.7
C226	M301A	CTG 81mm Illumination	222	2	0.9
C871	M853	CTG 81mm Illumination	220		
C542	M314	CTG 105mm Illumination	161	6	3.7
H183	M257 & FUZE M442	Rocket Flare 2.75	152	14	9.2
B647	M721	CTG 60mm Illumination	135		
D505	M48	Proj 155mm Illumination	119	1	0.8
C625	XM93	CTG 120mm Illumination	108		
CA07	M983	CTG 120mm IR Illum	49		
C484	M816 W/FUZE MTSQ M772	CTG 81mm IR Illum	25		
L310	M19A1, M19A2	Sig Illum Gren Para M	24	2	8.3
L305	M195	Sig Illum Gren	20		
L307	M159	Sig Illum Gren	19		
L601	M116A1	Sig Hand Gren	14		
L312	M127, M127A1	Sig Illum Gren	12		
CA46	M1105	120mm Mortar Illum	9		
L302	NA	Sig CTG White Flare	3		
Air Launched Smoke Munitions					
C624	XM929	CTG 120mm Smk WP	199	6	3.0
C479	M84A1	CTG 105mm Smk HC	169		
C276	M301A	CTG 81mm Smk WP	141	4	2.8
C454	M60, M60A1, M60A2, M60E1	CTG 105mm Smk WP	80		
C452	M84, M84A1, M84B1	CTG 105 mm Smk HC	56		
B477	M680	CTG 40 mm White Smk	25		
C453	M84, M84B1 W/FUZE MTSQ M501A1	105mm Red Smk F/How	20		
L341	M167	Sig Smk Gren	16		
D549	M116, M116B1	Proj 155mm Smk Red	12	2	16.7
Ground Use Simulators					
L594	M115A2	Sim Proj GND Burst	55	4	7.3
L596	M110	Sim Flash Arti	4		
Ground Use Smokes					
D446	M3	Smk Canister Green	48		
G955	M18	Gren Hand Violet	12		
G945	M18	Gren Hand Yellow	9		
L318	M65	Sig Smk Gren Green	9		
G940	M18	Gren Hand Green	8		
D445	M1	Smk Canister White	5		

Arti – artillery, GND – ground, Gren – grenade, Hex – Hexachloroethane,
How – howitzer, Illum – illumination, IR – infrared, M – mortar, Para – parachute,
Proj – projectile, Sig – signal, Sim – simulator, Smk – smoke, wht – white, WP – white phosphorous

Table A-2. Pyrotechnic munition devices found at Camp Edwards, Massachusetts from usage between 1911 through 1999 (USACE, 1999).

Military ID	Item	Filler Amount (g)	Military ID	Item	Filler Amount (g)
M80	Detonation Simulator	3	M118	Illumination Explosive Booby trap Simula-	5
M9A1	Aircraft Parachute Flare	544	M119	Whistling Explosive Booby trap Simulator	3
M81, M82 M83	Red, Yellow, Green Ground Flare	367	M110, M21	Flash Artillery Simulator	84, 43
M49, M49A1	Trip Flare	318, 20	M116A1	Hand Grenade Simulator	37
M48	Parachute Trip Flare	227	M22	Launching Anti-tank, Guided Missile, and	15
M72	Red Fusee	272	M27A1B1,M74, M74A1	Projectile Air Burst Simulator	62, 35
M1	HC Smoke Pot	4309 to 4990	M115A2	Projectile Ground Burst Simulator	65
M5	HC Smoke Pot	12,701	M8	HC Smoke Hand Grenade	532
M4A2	HC Floating Smoke Pot	10, 660	M18, M48	Colored Smoke Hand Grenade	326, 165
M17A1, M17A1B2	White Star Parachute Ground Signal	73	M583A1, M661, M662	40 mm Grenade White, Green, Red Star Parachute	93
M18A1, M18A1B2	White Star Cluster Ground Signal	113	M585	40 mm White Star Cluster	85
M19A1, M19A1B2, M19A2, M19A2B2	Green Star Parachute Ground Signal	73	M676, M680, M682	40 mm Yellow, White, Red Smoke	59, 80(Red)
M20A1, M20A1B2	Green Star Cluster Ground Signal	73	M713, M715, M716	40 mm Mortar Red, Green, Yellow Smoke Ground Marker	75
M21A1, M21A1B2	Amber Star Cluster Ground Signal	59	M721, M83A1, M83A2, M83A3	60 mm Mortar Illumination	222
M15A1, M15A1B2, M131	Red Star Parachute Ground Signal	73, 73 50	M722, M302, M302A1	60 mm Mortar White Phosphorous Smoke	340
M52A1, M52A1B2	Red Star Cluster Ground Signal	104	M301A1, M301A2, M301A3, M853A1	81 mm Mortar Illumination	635
M62, M168	Red Smoke Ground Signal	263, 18 or 28	M57, M57A1, M370, M375, M375A1, M375A2, M375A3	81 mm Mortar White Phosphorous Smoke	726
M64, M169	Yellow Smoke Ground Signal	263, 18	M819	81 mm Mortar White Phosphorous Smoke	1179
M65, M167	Green Smoke Ground Signal	263, 18 or 28	M335, M335A1, M335A2	4.2 in Mortar Illumination	1501
M66	Violet Smoke Ground Signal	263	M2, M2A1, M328, M328A1	4.2 in Mortar White Phosphorous Smoke	3402
M166	White Smoke Ground Signal	18 or 28	M314, M314A2, M314A2B1,	105 mm Projectile Illumination	790

Military ID	Item	Filler Amount (g)	Military ID	Item	Filler Amount (g)
M187, M188, M189, M190	Red, White, Green, Amber Illumination Ground Signal	4	M60, M60A1, M60A2	105 mm Projectile White Phosphorous Smoke	1751
M125, M158,	Green. Red, White Star Cluster	71	M84, M84A1	105 mm Projectile Colored Smoke	5580
M126A1, M127A1,	Red, White, Green Star Cluster	85	M118 Series	155 mm Projectile Illumination	1950
AN-M43A2, AN-	Aircraft Single Star Illumination	NA	M485 Series	155 mm Projectile Illumination	2635
AN-M53A2, AN-	Aircraft Double Star Illumination	NA	Mk 2A1, M105	155 mm Projectile Smoke	7362
M185, M186	Red, Various Personnel Distress Signal Kits	4	M110, M100A1, M110A2	155 mm Projectile White Phosphorous Smoke	7666
M128A1, M129A1,	Green, Red, Yellow Smoke Para-	57 or 70	M115	155 mm Projectile BE Smoke	11,721
M142	Atomic Explosion Simulator	50,000	M116, M116A1	155 mm Proj BE Smk (HC & Colored)	11,721
M117	Flash Explosive Booby trap Simu-	3	M116A1	155 mm Projectile HC Smoke	2472

Para – parachute, Proj – projectile, Sim – simulator, smk - smoke

Table A-3. Pyrotechnic procurement for Fiscal Year 2007 to 2009 by the US Army (US Army 2009).

DODIC Number	Military ID	Military Name	FY 2007	FY 2008	FY 2009
Air Launched Illumination Munitions					
BA04	M767	CTG 60 mm Illum IR	20,000	0	10,000
C871	M853	CTG 81mm Illum	0	90,000	11,000
CA07	M983	CTG 120mm IR Illum	7,000	14,000	13,000
L306	M158	Sig Hand Held Red Star Cluster	5,000	25,000	22,000
L307	M159	Sig Hand Held White Star Cluster	5,000	26,000	20,000
L311	M126A1	Sig Hand Held Red Parachute	0	14,000	13,000
L312	M127A1	Sig Hand Held White Parachute	5,000	96,000	83,000
L314	M125A1	Sig Hand Held Green Star Cluster	5,000	30,000	30,000
L305	M195	Sig Hand Held Green Parachute	0	4,000	5,000
L495	M49A1	Flare Surface Trip	34,000	39,000	35,000
Air Launched Smoke Munitions					
C624	XM929	CTG 120mm Smk WP	0	2,000	1,000
Ground Use Simulators					
L594	M115A2	Sim Proj GND Burst	396,000	179,000	211,000
L366	M74A1	Sim Proj Airburst	43,000	138,000	120,000
L598	M117	Sim Booby Trap Flash	183,000	99,000	59,000
L599	M118	Sim Booby Trap Illum	18,000	28,000	25,000
L600	M119	Sim Booby Trap Whistle	26,000	29,000	57,000
L601	M116A1	Sim Hand Grenade	79,000	247,000	242,000
L709	M25	Sim Target Hit	0	5,000	2,000
G937	M34	Sim Target Hit (Gren Hand & Rifle Smk WP	596,000	0	0
C752	M35	Sim Target Hit (Burster Projectile)	475,000	0	0
G810	M30	Sim Main Gun Tank (BODY PRAC HAND GREN M30)	289,000	234,000	147,000
NA	M311	Sim Dir/Indir Fire Cue	55,000	302,000	256,000
Ground Use Smokes					
D446	M8	Smk Pot Practice	1,000	1,000	2,000
G955	M18	Gren Hand Smk Violet	26,000	69,000	84,000
G950	M18	Gren Hand Smk Red	39,000	44,000	58,000
G945	M18	Gren Hand SmkYellow	86,000	104,000	82,000
G940	M18	Gren Hand Smk Green	65,000	138,000	126,000
G978	M82	Gren Smk Screen Practice	0	7,000	6,000
G982	M83	Gren Hand Smk Training	192,000	138,000	177,000

Dir – direct, GND – ground, Gren – grenade, Illum – illumination, Indir –indirect, IR – infrared, Sim – simulator, Smk – smoke, WP – white phosphorous

APPENDIX B: SNOW FILTER RESIDUE RESULTS

Table B-1. APPL Laboratories analytical ICP-MS results (mg/kg) for complete filter residue digestion samples.

Sample ID	Al	As	Ba	Be	B	Cd	Cr	Co	Cu	Fe	Pb	Mg	Mn	Mo	Ni	K	V	Zn
BLANK 1	15.0	0.340	3	ND	ND	ND	1.1	0.2	3.6	38	0.4	71	1.3	0.8	0.8	73	0.6	10
BLANK 2	11.7	0.150	2	ND	ND	ND	1.3	0.1	1.7	31	0.3	311	0.5	0.1	0.4	22	0.3	7.6
QC-21-1	12.4	868	5	870	7	867	974	993	964	999	872	1,020	951	858	962	73	962	797
QC-21-2	17.5	845	3	825	6	857	958	970	938	981	904	1,270	937	919	948	23	946	768
1-BF	470	ND	473	ND	140	0.3	50	0.4	1.3	911	2.2	563	15	ND	115	407	0.8	229
3F	556	ND	594	ND	414	ND	23	1.2	1.5	736	2.0	593	15	ND	54	652	0.7	411
4F	4,630	2.30	11,900	ND	5,130	7	814	0.8	5.9	2,850	27	11,000	65	ND	3,480	5,240	3.1	5,250
6F	2,800	1.80	7,310	ND	4,310	3	374	0.3	4.4	2,900	16	1,300	80	ND	1,630	3,110	2.9	3,950
9F	7,840	3.40	11,400	ND	8,820	0.3	8.1	1.2	6.4	2,490	6	4,620	44	ND	3.2	7,220	3.1	8,630
12F	123,000	1.50	27,100	ND	2,620	0.2	4.8	0.6	8,900	1,200	173	527	21	ND	7.9	1,960	14	2,510
14F	129,000	1.50	22,600	ND	3,470	0.5	4.9	0.6	9,090	1,190	160	593	24	ND	8.5	2,640	15	3,350
26F	4240	0.450	2,400	ND	1,700	0.2	1.8	5.2	1.3	1,330	0.4	345,000	50	ND	4.4	2,490	3.4	1,630
28F	6790	ND	1,850	ND	1,390	ND	1.5	4.8	1.1	1,800	0.3	323,000	45	ND	4.0	3,220	5.4	1,280
29F	11,300	3.90	18,700	ND	14,400	0.5	10	0.2	5.9	389	2.6	9,430	9.4	ND	1.9	11,200	1.0	14,100
32F	13,800	ND	1,450	ND	925	ND	1.8	7.0	4.0	3,240	0.8	287,000	37	ND	3.4	6,180	12	833
35F	5,560	ND	1,390	ND	764	ND	1.4	4.3	1.0	1,500	0.2	360,000	49	ND	4.4	2,790	5	716
39F	11,800	ND	1,340	ND	491	ND	1.4	7.7	2	2,600	0.2	326,000	37	ND	3.3	5,230	10	451
42F	1,460	17.4	583	ND	1,280	0.4	8.4	0.4	35	683	28	43,800	82	ND	4.3	3,030	0.9	1,350
45F	1,090	24.3	345	ND	316	0.3	7.9	0.5	34	820	30	54,600	84	0.3	4.7	2,040	1.4	441
46-1F	982	11.0	599	ND	714	0.3	7.2	0.3	28	536	22	32,700	69	ND	2.6	2,410	0.9	764
46-2F	871	16.0	470	ND	419	0.3	7.7	0.4	31	592	22	37,300	69	ND	3.1	893	0.9	528
47F	9380	3.30	19,000	ND	11,800	6.0	600	0.3	3.8	663	19	6,790	40	ND	1,950	9,900	1.3	11,400
51F	137,000	0.44	288	ND	530	0.3	3.2	0.6	11,600	959	203	347	26	0.1	10	440	17	505

Sample ID	Al	As	Ba	Be	B	Cd	Cr	Co	Cu	Fe	Pb	Mg	Mn	Mo	Ni	K	V	Zn
53F	158,000	0.82	517	ND	313	0.2	5.7	1.8	12,600	5,070	184	949	92	0.2	15	274	21	356
55F	115,000	0.5	901	ND	1,190	0.2	2.6	0.4	9,160	685	138	340	17	ND	7.4	893	11	1,150
57F	78,100	0.56	290	ND	449	ND	3.5	0.8	6,060	1,590	72	589	46	0.1	7.2	399	9.0	425

ND = not detected

Table B-2. CRREL analytical ICP-OES results (mg/kg) for filter residue samples.

Sample ID	Digested/ Analyzed	Analysis Date	Al	Sb	As	Ba	Be	Cd	Ca	Cr	Co	Cu	Fe	Pb	Mn	Mg	Ni	K	Se	Ag	Na	Tl	V	Zn
CEA4-3-1AF-Rep1	EL/CRREL	6/1/10	1810	72.1	44.5	229	42.6	50.1	1280	99.4	83.4	86.4	2760	81.6	228	1210	144	963	46.0	26.9	872	36.3	85.6	209
CEA4-3-1BF	EL/CRREL	6/1/10	79.7	0.196	0.223	46.4	ND	ND	72.2	4.97	ND	ND	181	ND	ND	169	29.0	98.9	0.196	ND	80.3	ND	0.065	ND
CEA4-3-4F	EL/CRREL	6/1/10	784	5.53	ND	4580	0.112	ND	1180	873	ND	ND	1600	20.9	33.4	13,090	3280	512	ND	ND	132	ND	0.596	448
CEA4-3-9F	EL/CRREL	6/1/10	484	ND	0.140	22.0	0.020	ND	566	ND	ND	ND	799	ND	ND	275	ND	93.4	ND	ND	174	ND	0.800	21.3
CEA4-3-12F	EL/CRREL	6/1/10	147,000	1.40	2.85	36,700	0.130	ND	1010	ND	ND	11,400	1150	273	4.86	362	ND	63.0	ND	ND	169	ND	15.7	32.6
CEA4-3-26F	EL/CRREL	6/1/10	4900	0.323	0.385	113	0.108	ND	242	ND	ND	ND	900	ND	31.6	296,000	ND	1790	ND	ND	1300	ND	2.71	2.14
CEA4-3-29F	EL/CRREL	6/1/10	298	0.400	ND	335	0.020	ND	226	ND	ND	ND	265	ND	ND	3790	ND	267	ND	ND	759	ND	0.240	323
CEA4-3-33F	EL/CRREL	6/1/10	6100	0.223	0.477	161	0.127	ND	354	ND	ND	ND	1230	ND	23.5	236,000	ND	2810	ND	ND	1370	ND	3.47	ND
CEA4-3-42F	EL/CRREL	6/1/10	393	2370	8.01	24.4	0.057	ND	1200	ND	ND	15.4	87.2	ND	97.2	73,800	ND	889	ND	ND	140	ND	0.271	83.3
CEA4-3-47F	EL/CRREL	6/1/10	569	16.8	ND	12,200	ND	ND	3160	2130	ND	ND	785	ND	ND	22,700	7920	766	ND	ND	865	ND	ND	723
CEA4-3-51F	EL/CRREL	6/1/10	115,000	2.24	2.41	5160	0.178	ND	703	ND	ND	11,400	834	279	6.34	2912	ND	45.3	ND	ND	116	ND	15.4	26.9
CEA4-3-1AF-Rep1	EL/CRREL	9/18/10	1710	64.1	38.6	225	41.0	60.0	1310	99.1	87.9	83.6	2960	83.2	210	1200	138	830	40.3	33.3	744	45.8	78.0	209
CEA4-3-1AF-Rep2	EL/CRREL	9/18/10	1820	72.3	45.1	254	43.3	50.6	1290	100	84.2	87.3	2790	81.8	228	1210	145	968	45.9	26.9	859	36.8	86.1	211
CEA4-3-1AF-Rep3	EL/CRREL	9/18/10	1020	0.382	1.06	68.9	0.055	ND	487	10.8	ND	ND	2270	ND	21.2	463	43.1	211	ND	ND	90.4	ND	1.71	17.6
CEA4-3-1BF	EL/CRREL	9/18/10	1720	65.5	38.7	224	40.6	60.1	1290	98.8	88.1	83.4	2930	83.7	2089	1190	138	826	40.6	31.5	742	45.6	78.3	209
CEA4-3-4F	EL/CRREL	9/18/10	982	0.273	0.473	77.6	ND	ND	500	21.7	1.38	6.48	2430	3.11	31.4	466	49.9	191	ND	ND	66.0	ND	1.53	28.8
CEA4-3-9F	EL/CRREL	9/18/10	76.4	0.079	0.052	51.5	ND	ND	72.9	13.4	ND	2.88	192	0.615	2.10	166	34.1	89.7	0.039	ND	35.0	0.052	ND	5.09
CEA4-3-12F	EL/CRREL	9/18/10	752	5.89	ND	4100	0.019	ND	1170	771	2.46	6.47	1690	30.9	41.5	12,800	2860	443	ND	ND	64.6	ND	0.503	436
CEA4-3-26F	EL/CRREL	9/18/10	459	ND	ND	35.6	ND	ND	576	0.880	0.140	5.06	847	1.60	13.7	275	1.02	85.6	ND	ND	103	0.040	0.660	33.5
CEA4-3-29F	EL/CRREL	9/18/10	141,000	0.843	2.53	30,500	ND	ND	1000	2.64	ND	9650	1200	242	18.6	346	8.63	57.1	ND	ND	76.5	ND	14.4	45.7
CEA4-3-33F	EL/CRREL	9/18/10	4510	0.246	0.447	108	ND	ND	249	0.816	2.34	3.00	952	3.27	37.9	289,000	4.25	1500	ND	ND	966	ND	2.37	12.0
CEA4-3-42F	EL/CRREL	9/18/10	282	0.260	ND	322	ND	ND	234	0.400	ND	4.96	279	0.240	3.64	3730	0.340	227	ND	ND	568	ND	0.140	318

Sample ID	Digested/ Analyzed	Analysis Date	Al	Sb	As	Ba	Be	Cd	Ca	Cr	Co	Cu	Fe	Pb	Mn	Mg	Ni	K	Se	Ag	Na	Tl	V	Zn
CEA4-3-47F	EL/CRREL	9/18/10	5790	0.270	ND	158	ND	ND	359	0.843	2.32	3.21	1310	4.49	31.4	231,000	3.87	2400	ND	ND	1110	ND	3.15	2.04
CEA4-3-51F	EL/CRREL	9/18/10	372	2080	6.80	31.8	ND	ND	1220	6.27	ND	22.1	93.1	ND	93.1	71,700	3.79	756	ND	ND	58.2	0.242	0.242	89.1
CEA4-3-1AF-Rep2	EL/CRREL	6/1/10	539	16.7	ND	11,000	ND	ND	3250	1950	1.36	40.8	818	54.9	102	22,400	7060	683	ND	ND	430	ND	ND	785
CEA4-3-1AF-Rep3	EL/CRREL	6/1/10	110,000	1.70	1.51	3640	ND	ND	693	2.24	ND	9710	867	241	17.5	282	10.5	46.5	ND	ND	72.3	ND	14.0	37.3

ND = not detected, NR = not reported, Rep = field replicates

Table B-3. EL analytical ICP-MS results (mg/kg) for filter residue samples.

Sample ID	Test	Rep	Sb	As	Ba	Be	Cd	Cr	Co	Cu	Pb	Mn	Mo	Ni	Se	Ag	Tl	Sn	V	Zn
CEA 4 - 3 # 1 - A F	M18 Test 1	1	0.274	0.43	89.2	ND	ND	21.7	0.947	3.05	2.43	28.1	ND	43.8	ND	ND	ND	5.69	1.44	22.4
CEA 4 - 3 # 1 - B F	M18 Test 1	2	0.105	ND	57.9	ND	ND	14.3	ND	0.486	0.381	2.08	ND	33.9	ND	ND	ND	4.53	0.108	3.82
CEA 4 - 3 # 3 - A F	M18 Test 3	1	0.660	0.117	59.6	ND	ND	17.8	0.143	0.432	0.749	5.12	ND	33.6	ND	ND	ND	4.79	0.218	8.45
CEA 4 - 3 # 3 - B F	M18 Test 3	2	0.292	1.18	100	ND	ND	8.28	2.59	7.47	8.78	108	0.251	12.7	0.364	ND	ND	1.75	4.47	67.2
CEA 4 - 3 # 4F	M18 Test 4	1	0.215	0.417	5570	ND	0.739	888	0.834	3.37	30.4	39.6	0.175	3050	0.331	3.53	ND	18.6	1.27	368
CEA 4 - 3 # 6F	M18 Test 6	1	0.404	0.639	1690	ND	0.360	311	1.11	4.20	12.8	60.5	0.123	1040	0.182	1.85	ND	6.89	1.81	172
CEA 4 - 3 # 9F	Background	1	0.159	0.233	42.2	ND	ND	0.925	0.258	2.11	1.34	13.6	ND	1.18	ND	ND	ND	4.78	0.766	29.4
CEA 4 - 3 # 10F	Background	2	2.87	5.50	809	0.326	0.796	20.3	6.28	42.2	33.6	313	1.79	18.4	1.73	0.284	0.108	37.2	20.0	514
CEA 4 - 3 # 12F	M21 Test 1	1	1.16	0.527	57,700	ND	0.192	3.44	0.661	13,000	282	23.6	0.370	10.9	1.03	0.349	ND	23.8	17.4	56.0
CEA 4 - 3 # 14F	M21 Test 3	3	1.28	0.528	6250	ND	0.545	3.46	0.778	11,900	133	27.6	0.335	11.7	0.581	0.424	ND	23.1	21.6	46.5
CEA 4 - 3 # 26F	M127A1 Test 1	1	0.237	ND	125	ND	ND	0.974	2.24	1.13	0.222	38.8	ND	4.38	ND	ND	ND	3.01	2.45	10.5
CEA 4 - 3 # 28F	M127A1 Test 1	3	0.121	0.239	263	ND	ND	1.06	3.75	1.92	0.175	44.3	ND	4.79	ND	ND	ND	2.99	1.72	98.4
CEA 4 - 3 # 29F	M127A1 Test 1	1	0.328	0.101	400	ND	ND	0.443	ND	0.641	0.435	3.24	ND	0.374	ND	ND	ND	4.84	0.228	248
CEA 4 - 3 # 31F	M127A1 Test 1	3	3.22	1.24	755	0.124	0.287	6.15	2.07	11.2	5.92	70.9	0.433	4.72	ND	ND	ND	47.0	4.67	545
CEA 4 - 3 # 32F	M127A1 Test 1	1	ND	0.168	283	ND	ND	0.914	4.51	3.20	0.691	30	ND	3.10	0.204	ND	ND	3.00	3.63	70.0
CEA 4 - 3 # 33F	M127A1 Test 2	1	0.237	ND	187	ND	ND	0.855	1.91	0.752	0.233	24.8	ND	3.46	ND	ND	ND	2.83	2.76	1.93
CEA 4 - 3 # 35F	M127A1 Test 2	3	0.138	0.108	340	ND	ND	0.796	2.04	1.22	ND	33.1	ND	3.80	ND	ND	ND	3.13	1.44	6.48
CEA 4 - 3 # 36F	M127A1 Test 2	1	2.04	0.723	1040	ND	0.174	4.15	1.4	5.98	5.57	56.2	0.482	3.84	ND	0.138	ND	51.8	3.32	785
CEA 4 - 3 # 37F	M127A1 Test 2	2	5.01	1.12	1030	ND	0.192	5.92	1.27	7.91	4.83	55.1	0.564	3.86	25.6	0.115	ND	49.6	2.69	711
CEA 4 - 3 # 38F	M127A1 Test 2	3	420	0.745	1250	ND	0.226	2.90	1.08	5.01	9.66	38	0.307	2.50	4.26	ND	ND	30.3	2.1	961
CEA 4 - 3 # 39F	M127A1 Test 2	1	ND	ND	575	ND	ND	1.29	5.99	1.97	0.36	29.3	ND	3.2	ND	ND	ND	2.19	8.84	94.7
CEA 4 - 3 # 42F	M117 Test 1	1	*	6.5	38.6	ND	ND	5.99	ND	17.1	0.376	92.9	ND	3.52	ND	ND	0.118	0.180	0.272	66.7
CEA 4 - 3 # 44F	Background	2	144	18.7	27,100	0.295	2.84	100	21.5	280	176	942	12.8	97.1	ND	2.33	0.55	1040	61.2	22,400

Sample ID	Test	Rep	Sb	As	Ba	Be	Cd	Cr	Co	Cu	Pb	Mn	Mo	Ni	Se	Ag	Tl	Sn	V	Zn
CEA 4 - 3 # 45F	M117 Test 1	1	8050	8.72	102	ND	0.416	10.7	0.392	57.6	14.2	180	ND	10.5	0.946	ND	0.405	0.529	0.752	320
CEA 4 - 3 # 46F	M117 Test 2	1	6370	6.03	77.1	ND	0.232	6.58	0.236	42.7	15.1	128	ND	6.96	0.55	ND	0.372	0.525	0.379	156
CEA 4 - 3 # 46F	M117 Test 2	1	*	5.66	124	ND	0.143	6.71	0.192	42.3	0.219	112	ND	4.17	ND	ND	0.286	0.494	0.361	163
CEA 4 - 3 # 46 - 2F	M117 Test 2	2	4950	5.49	135	ND	0.236	7.46	0.225	50.2	6.14	119	ND	5.51	0.31	ND	0.315	0.479	0.415	164
CEA 4 - 3 # 47F	M18 Test 6	1	3.57	0.322	13,800	ND	2.24	2130	0.382	5.31	68.2	84.3	0.365	6810	0.77	12.0	ND	40.0	0.851	628
CEA 4 - 3 # 49F	M18 Test 6	3	25.7	0.831	11,000	ND	2.29	1890	0.667	10.0	59.5	114	0.320	5500	3.74	12.4	ND	48.9	1.13	669
CEA 4 - 3 # 51F	M18 Test 6	1	2.02	0.285	7230	ND	0.146	3.03	0.574	13,700	388	21.1	0.242	13.1	0.114	0.374	ND	28.7	17.3	39.1
CEA 4 - 3 # 53F	M21 Test 2	3	1.93	0.811	4850	0.106	0.183	4.37	1.69	11,400	167	79.6	0.323	14.0	0.289	0.454	ND	24.6	20.7	58.2
CEA 4 - 3 # 55F	M21 Test 3	1	1.9	0.421	6500	0.109	0.231	4.6	1.03	20,200	141	32.9	0.327	20.7	0.319	0.752	ND	44.2	29.7	57.7
CEA 4 - 3 # 56F	M21 Test 3	2	1.59	0.424	6200	0.116	0.205	4.37	1.18	16,900	163	46.8	0.309	17.8	0.278	0.589	ND	36.9	27.0	58.1
CEA 4 - 3 # 57F	M21 Test 3	3	2.48	0.636	3440	ND	0.171	4.13	1.38	12,300	71.1	61.8	0.265	14.9	0.264	0.494	ND	23.4	19.7	41.7

*result above linear calibration range, quantification unreliable, ND = not detected.

APPENDIX C: SNOW SAMPLE RESULTS

Table C-1. CRREL analytical ICP-OES results (mg/L) for filtered snow samples.

Sample ID	Weight (g)	Ag	Al	As	Ba	Be	Ca	Co	Cr	Cu	Fe	K	Mg	Mo	Na	Ni	Pb	Sb	Se	Tl	V	Zn
CEA4-3-1	13823.8	ND	0.054	0.0009	0.418	ND	0.897	ND	ND	ND	0.013	20.0	4.17	NA	0.269	ND	ND	ND	0.001	ND	ND	ND
CEA4-3-2	13400.3	ND	0.023	0.001	0.276	ND	1.04	ND	ND	ND	0.005	18.5	6.17	NA	0.358	ND	ND	ND	ND	ND	ND	ND
CEA4-3-3	12839.3	ND	0.013	0.0008	0.116	ND	0.710	ND	ND	ND	0.007	14.5	3.45	NA	0.225	ND	ND	ND	ND	ND	ND	ND
CEA4-3-4	1465.3	ND	0.028	ND	0.879	ND	0.888	ND	ND	ND	0.004	51.4	8.64	NA	0.810	ND	ND	ND	ND	ND	ND	ND
CEA4-3-5	3014.2	ND	0.020	0.0002	0.503	ND	1.20	ND	ND	ND	0.005	30.1	9.22	NA	0.650	ND	ND	0.003	ND	ND	ND	ND
CEA4-3-6	6944.0	ND	0.025	ND	0.348	ND	0.837	ND	ND	ND	ND	25.1	5.90	NA	0.483	ND	ND	0.003	ND	ND	ND	ND
CEA4-3-9	1634.2	ND	0.018	ND	ND	ND	1.33	ND	ND	ND	0.013	ND	0.093	NA	1.00	ND	ND	ND	ND	ND	ND	ND
CEA4-3-10	1744.5	ND	0.018	ND	ND	ND	1.21	ND	ND	ND	0.016	ND	0.087	NA	1.01	ND	ND	ND	ND	ND	ND	ND
CEA4-3-11	3147.0	ND	0.009	ND	ND	ND	1.13	ND	ND	ND	0.017	ND	0.103	NA	0.577	ND	ND	ND	ND	ND	ND	ND
CEA4-3-12	1995.9	ND	0.082	ND	101	ND	1.09	ND	ND	ND	0.002	ND	0.074	NA	0.740	ND	ND	ND	ND	ND	ND	ND
CEA4-3-13	1595.7	ND	8.880	ND	167	ND	1.00	ND	ND	ND	0.003	ND	0.084	NA	0.804	ND	ND	ND	ND	ND	ND	ND
CEA4-3-14	1005.0	ND	0.632	ND	189	ND	1.39	ND	ND	ND	ND	ND	0.108	NA	1.19	ND	ND	ND	ND	ND	ND	ND
CEA4-3-26	1324.0	ND	0.005	0.005	0.524	0.0001	0.648	ND	ND	ND	0.000	5.62	0.150	NA	652	ND	ND	0.006	0.007	ND	0.001	ND
CEA4-3-27	587.1	ND	0.016	0.022	2.02	ND	0.631	ND	ND	ND	0.001	19.8	0.018	NA	2130	ND	ND	ND	0.036	ND	0.012	ND
CEA4-3-28	1276.7	ND	0.006	0.005	0.599	ND	0.435	ND	ND	ND	0.015	7.88	1.58	NA	671	ND	ND	ND	0.011	ND	0.002	ND
CEA4-3-29	914.0	ND	0.088	ND	0.069	ND	0.268	ND	ND	ND	0.005	0.057	2.92	NA	1.40	ND	ND	ND	0.001	ND	ND	ND
CEA4-3-30	602.0	ND	0.041	0.0005	0.011	ND	0.180	ND	ND	ND	ND	0.039	3.68	NA	1.41	ND	ND	ND	ND	ND	ND	ND
CEA4-3-31	1157.4	ND	0.015	ND	ND	ND	0.266	ND	ND	ND	ND	0.006	1.79	NA	0.943	ND	ND	ND	ND	ND	ND	ND
CEA4-3-32	4845.2	ND	0.176	0.025	2.56	ND	0.836	ND	ND	ND	ND	29.0	ND	NA	2040	ND	ND	ND	0.042	ND	0.013	ND
CEA4-3-33	1466.8	ND	0.067	0.007	1.51	ND	0.716	ND	ND	ND	ND	12.4	0.022	NA	811	ND	ND	ND	0.010	ND	0.004	ND
CEA4-3-34	558.8	ND	1.573	0.022	3.02	ND	0.779	ND	ND	ND	ND	31.8	0.009	NA	1690	ND	ND	0.002	0.035	ND	0.014	ND
CEA4-3-35	1089.2	ND	0.005	0.009	1.26	0.0002	0.801	ND	ND	ND	ND	9.71	0.138	NA	699	ND	ND	ND	0.012	ND	0.003	ND

Sample ID	Weight (g)	Ag	Al	As	Ba	Be	Ca	Co	Cr	Cu	Fe	K	Mg	Mo	Na	Ni	Pb	Sb	Se	Tl	V	Zn
CEA4-3-36	997.1	ND	0.013	ND	ND	ND	0.293	ND	ND	ND	0.005	0.205	2.50	NA	2.33	ND	ND	0.002	ND	ND	ND	ND
CEA4-3-37	1060.1	ND	0.010	ND	ND	ND	0.310	ND	ND	ND	0.006	0.099	1.44	NA	1.64	ND	ND	0.001	ND	ND	ND	ND
CEA4-3-38	971.8	ND	0.022	ND	ND	ND	0.251	ND	ND	ND	ND	0.067	2.09	NA	1.90	ND	ND	ND	ND	ND	ND	ND
CEA4-3-39	3725.7	ND	0.113	0.030	4.05	ND	0.838	ND	ND	ND	ND	33.8	ND	NA	1810	ND	ND	ND	0.051	ND	0.013	ND
CEA4-3-42	5246.2	ND	0.111	0.083	ND	0.0003	2.95	ND	ND	ND	ND	227	38.3	NA	6.22	ND	ND	39.0	0.004	ND	0.001	ND
CEA4-3-43	5844.5	ND	0.128	0.072	ND	ND	3.35	ND	ND	ND	ND	173	31.1	NA	7.18	ND	ND	33.4	0.004	ND	0.001	ND
CEA4-3-44	2405.1	ND	0.046	ND	ND	0.0000	0.300	ND	ND	ND	0.006	0.123	0.037	NA	1.36	ND	ND	0.013	ND	ND	ND	ND
CEA4-3-45	1454.9	ND	0.119	0.108	ND	0.0004	3.60	ND	ND	ND	ND	408	28.4	NA	5.06	ND	ND	43.8	0.004	ND	0.001	ND
CEA4-3-46-1	6209.7	ND	0.122	0.081	ND	0.0001	4.02	ND	ND	ND	ND	208	36.9	NA	9.52	ND	ND	32.2	0.002	ND	0.000	ND
CEA4-3-46-2	1361.0	ND	0.141	0.065	ND	0.0000	3.21	ND	ND	ND	ND	41.4	36.4	NA	2.52	ND	ND	59.2	0.002	ND	0.001	ND
CEA4-3-46-3	1102.8	ND	0.162	0.118	ND	0.0004	3.78	ND	ND	ND	ND	389	28.5	NA	7.65	ND	ND	49.6	0.002	ND	0.002	ND
CEA4-3-47	1547.5	ND	0.014	ND	0.242	ND	0.713	ND	ND	ND	0.010	29.7	4.88	NA	0.911	ND	ND	0.005	ND	ND	ND	ND
CEA4-3-48	648.3	ND	0.029	0.0001	0.651	0.0002	1.28	ND	ND	ND	0.004	107	13.0	NA	1.27	ND	ND	0.012	ND	ND	ND	ND
CEA4-3-49	1284.3	ND	0.014	ND	0.260	ND	0.766	ND	ND	ND	0.002	36.9	5.51	NA	0.910	ND	ND	0.017	ND	ND	ND	ND
CEA4-3-51	1931.2	ND	34.3	ND	391	0.0001	0.526	ND	ND	ND	ND	0.119	0.078	NA	1.08	ND	ND	0.002	ND	ND	ND	ND
CEA4-3-52	2347.3	ND	1.37	ND	306	0.0001	1.05	ND	ND	ND	ND	0.176	0.246	NA	1.23	ND	ND	0.000	ND	ND	ND	ND
CEA4-3-53	3381.2	ND	0.265	ND	284	0.0001	1.37	ND	ND	ND	ND	0.181	0.225	NA	1.01	ND	ND	0.001	ND	ND	ND	ND
CEA4-3-55	2281.1	ND	24.2	ND	223	ND	0.617	ND	ND	ND	0.001	0.093	0.097	NA	0.912	ND	ND	0.001	ND	ND	ND	ND
CEA4-3-56	2667.8	ND	18.9	ND	242	ND	0.788	ND	ND	ND	ND	0.247	0.146	NA	0.857	ND	ND	ND	ND	ND	ND	ND
CEA4-3-57	3785.8	ND	13.9	ND	206	ND	1.90	ND	ND	ND	ND	0.235	0.217	NA	1.46	ND	ND	0.004	ND	ND	ND	ND

NA = not analyzed, ND = not detected

Table C-2. EL analytical ICP-MS results (mg/L) for filtered snow samples.

Sample ID	Sb	As	Ba	Be	Cd	Cr	Co	Cu	Pb	Mn	Mo	Ni	Se
CEA 4-3 #1	0.0016	<0.0004	0.440	<0.0004	<0.0004	0.0226	0.0012	0.0016	0.0006	0.0639	<0.0004	0.013	0.0004
CEA 4-3 #2	0.0007	<0.0004	0.496	<0.0004	<0.0004	0.0207	0.0012	0.0005	0.0005	0.0765	<0.0004	0.0294	0.0005
CEA 4-3 #3	0.0014	<0.0004	0.122	<0.0004	<0.0004	0.0057	0.0005	0.0017	0.0006	0.0458	<0.0004	0.0031	<0.0004
CEA 4-3 #4	<0.0004	<0.0004	0.908	<0.0004	<0.0004	0.0717	<0.0004	0.0009	0.0005	0.0064	<0.0004	0.0121	0.0004
CEA 4-3 #5	0.0024	<0.0004	0.585	<0.0004	<0.0004	0.032	<0.0004	0.0007	<0.0004	0.0174	<0.0004	0.0049	<0.0004
CEA 4-3 #6	0.0035	<0.0004	0.417	<0.0004	<0.0004	0.0448	<0.0004	0.0008	<0.0004	0.0071	<0.0004	0.0063	0.0004
CEA 4-3 #9	<0.0004	<0.0004	0.041	<0.0004	<0.0004	<0.0004	<0.0004	0.0008	0.0005	0.0106	<0.0004	0.0005	<0.0004
CEA 4-3 #10	<0.0004	<0.0004	0.015	<0.0004	<0.0004	<0.0004	<0.0004	0.0008	<0.0004	0.0099	<0.0004	<0.0004	<0.0004
CEA 4-3 #11	<0.0004	<0.0004	0.023	<0.0004	<0.0004	<0.0004	<0.0004	0.0007	<0.0004	0.0094	<0.0004	<0.0004	0.0005
CEA 4-3 #12	0.26	<0.200	107	<0.200	<0.200	<0.200	<0.200	<0.200	<0.200	<0.200	<0.200	<0.200	<0.200
CEA 4-3 #13	0.227	<0.200	171	<0.200	<0.200	<0.200	<0.200	<0.200	<0.200	<0.200	<0.200	<0.200	<0.200
CEA 4-3 #14	0.201	<0.200	200	<0.200	<0.200	<0.200	<0.200	<0.200	<0.200	<0.200	<0.200	<0.200	<0.200
CEA 4-3 #26	0.0064	<0.0004	0.654	<0.0004	<0.0004	0.0037	<0.0004	0.0005	<0.0004	<0.0004	<0.0004	<0.0004	0.0006
CEA 4-3 #27	0.0005	<0.0004	2.270	<0.0004	<0.0004	0.0198	<0.0004	0.0036	0.0027	<0.0004	0.00052	<0.0004	0.0012
CEA 4-3 #28	0.0014	<0.0004	0.716	<0.0004	<0.0004	0.006	<0.0004	0.0008	<0.0004	<0.0004	<0.0004	<0.0004	<0.0004
CEA 4-3 #29	<0.0004	<0.0004	0.133	<0.0004	<0.0004	<0.0004	<0.0004	0.0013	<0.0004	0.0017	<0.0004	<0.0004	<0.0004
CEA 4-3 #30	0.0006	<0.0004	0.096	<0.0004	<0.0004	<0.0004	<0.0004	0.0015	<0.0004	0.0013	<0.0004	<0.0004	<0.0004
CEA 4-3 #31	<0.0004	<0.0004	0.038	<0.0004	<0.0004	<0.0004	<0.0004	0.0007	<0.0004	0.002	<0.0004	<0.0004	<0.0004
CEA 4-3 #32	0.0004	0.0012	2.900	<0.0004	<0.0004	0.021	0.0004	0.017	0.0021	0.0007	0.00057	<0.0004	0.0015
CEA 4-3 #33	<0.0004	<0.0004	1.690	<0.0004	<0.0004	0.006	<0.0004	0.0032	0.0006	<0.0004	<0.0004	<0.0004	0.0004

Sample ID	Sb	As	Ba	Be	Cd	Cr	Co	Cu	Pb	Mn	Mo	Ni	Se
CEA 4-3 #34	0.0031	0.0008	3.090	<0.0004	<0.0004	0.019	0.0004	0.0387	0.0025	0.0005	0.0008	<0.0004	0.0015
CEA 4-3 #35	<0.0004	<0.0004	1.410	<0.0004	<0.0004	0.007	<0.0004	0.0007	<0.0004	<0.0004	<0.0004	<0.0004	0.0004
CEA 4-3 #36	0.0007	<0.0004	0.073	<0.0004	<0.0004	<0.0004	<0.0004	0.002	<0.0004	0.002	<0.0004	<0.0004	<0.0004
CEA 4-3 #37	<0.0004	<0.0004	0.022	<0.0004	<0.0004	<0.0004	<0.0004	0.0007	<0.0004	0.0026	<0.0004	<0.0004	<0.0004
CEA 4-3 #38	<0.0004	<0.0004	0.021	<0.0004	<0.0004	<0.0004	<0.0004	<0.0004	<0.0004	0.002	<0.0004	<0.0004	<0.0004
CEA 4-3 #39	0.0005	0.0014	4.450	<0.0004	<0.0004	0.022	0.0007	0.0036	<0.0004	0.00053	0.00071	<0.0004	0.0012
CEA 4-3 #42	34.8	0.0745	0.084	<0.0004	<0.0004	0.006	<0.0004	0.0046	0.0008	0.0079	<0.0004	0.0028	0.0051
CEA 4-3 #43	30.4	0.0649	0.052	<0.0004	<0.0004	0.005	<0.0004	0.0057	0.0009	0.0107	0.0004	0.0025	0.0041
CEA 4-3 #44	0.0274	<0.0004	0.050	<0.0004	<0.0004	<0.0004	<0.0004	0.0019	<0.0004	0.0028	<0.0004	<0.0004	<0.0004
CEA 4-3 #45	38.9	0.0929	0.108	<0.0004	<0.0004	0.009	<0.0004	0.0013	<0.0004	0.003	0.001	0.0021	0.0066
CEA 4-3 #46-1	28.1	0.0709	0.056	<0.0004	<0.0004	0.007	<0.0004	0.004	0.0009	0.0158	<0.0004	0.0029	0.0039
CEA 4-3 #46-2	54.8	0.0598	0.096	<0.0004	<0.0004	0.002	<0.0004	0.0034	0.0008	0.0073	<0.0004	0.0016	0.0047
CEA 4-3 #46-3	44.1	0.1	0.102	<0.0004	<0.0004	0.012	<0.0004	0.0023	0.0008	0.0055	0.0009	0.0021	0.0061
CEA 4-3 #47	0.0213	<0.0004	0.323	<0.0004	<0.0004	0.028	<0.0004	0.0028	<0.0004	0.0042	<0.0004	0.0496	<0.0004
CEA 4-3 #48	0.0174	<0.0004	0.687	<0.0004	<0.0004	0.059	<0.0004	0.0022	0.0004	0.0047	<0.0004	0.16	<0.0004
CEA 4-3 #49	0.0163	<0.0004	0.343	<0.0004	<0.0004	0.028	<0.0004	0.0016	<0.0004	0.0035	<0.0004	0.0546	<0.0004
CEA 4-3 #51	0.548	<0.200	335	<0.200	<0.200	<0.200	<0.200	<0.200	<0.200	<0.200	<0.200	<0.200	<0.200
CEA 4-3 #52	0.442	<0.200	336	<0.200	<0.200	<0.200	<0.200	<0.200	<0.200	<0.200	<0.200	<0.200	<0.200
CEA 4-3 #53	0.379	<0.200	307	<0.200	<0.200	<0.200	<0.200	<0.200	<0.200	<0.200	<0.200	<0.200	<0.200
CEA 4-3 #55	0.36	<0.200	253	<0.200	<0.200	<0.200	<0.200	0.304	<0.200	<0.200	<0.200	<0.200	<0.200
CEA 4-3 #56	0.322	<0.200	264	<0.200	<0.200	<0.200	<0.200	<0.200	<0.200	<0.200	<0.200	<0.200	<0.200

Sample ID	Sb	As	Ba	Be	Cd	Cr	Co	Cu	Pb	Mn	Mo	Ni	Se
CEA 4-3 #57	0.277	<0.200	214	<0.200	<0.200	<0.200	<0.200	<0.200	<0.200	<0.200	<0.200	<0.200	<0.200

Table C-2 (continued). ERDC-EL analytical ICP-MS results (mg/L) for filtered snow samples.

Sample ID	Ag	Tl	V	Zn	Chlorate	Chloride	Chlorite	Per-chlorate
CEA 4-3 #1	<0.0004	<0.0004	<0.0004	0.056	8.2	6.4	< 0.5	< 1.0
CEA 4-3 #2	<0.0004	<0.0004	<0.0004	0.079	15.2	7.2	< 0.5	< 1.0
CEA 4-3 #3	<0.0004	<0.0004	<0.0004	0.024	5.2	5.8	< 0.5	< 1.0
CEA 4-3 #4	<0.0004	<0.0004	0.0005	0.009	35.7	11.6	< 0.5	< 1.0
CEA 4-3 #5	<0.0004	<0.0004	<0.0004	0.011	12.5	9.9	< 0.5	< 1.0
CEA 4-3 #6	<0.0004	<0.0004	<0.0004	0.005	12.6	5.1	< 0.5	< 1.0
CEA 4-3 #9	<0.0004	<0.0004	<0.0004	0.013	< 0.5	1.6	< 0.5	< 1.0
CEA 4-3 #10	<0.0004	<0.0004	<0.0004	0.014	< 0.5	1.6	< 0.5	< 1.0
CEA 4-3 #11	<0.0004	<0.0004	<0.0004	0.014	< 0.5	1.1	< 0.5	< 1.0
CEA 4-3 #12	<0.200	<0.200	<0.200	2.38	< 0.5	1.2	< 0.5	< 1.0
CEA 4-3 #13	<0.200	<0.200	<0.200	3.70	< 0.5	1.3	< 0.5	< 1.0
CEA 4-3 #14	<0.200	<0.200	<0.200	2.27	< 0.5	1.7	< 0.5	< 1.0
CEA 4-3 #26	<0.0004	<0.0004	0.0012	0.003	< 0.5	1.8	< 0.5	< 1.0
CEA 4-3 #27	<0.0004	<0.0004	0.0139	0.012	< 0.5	3	< 0.5	< 1.0
CEA 4-3 #28	<0.0004	<0.0004	0.0024	0.002	< 0.5	1.7	< 0.5	< 1.0
CEA 4-3 #29	<0.0004	<0.0004	<0.0004	0.004	< 0.5	0.82	< 0.5	< 1.0
CEA 4-3 #30	<0.0004	<0.0004	<0.0004	0.004	< 0.5	0.76	< 0.5	< 1.0
CEA 4-3 #31	<0.0004	<0.0004	<0.0004	0.003	< 0.5	0.82	< 0.5	< 1.0

Sample ID	Ag	Tl	V	Zn	Chlorate	Chloride	Chlorite	Per-chlorate
CEA 4-3 #32	<0.0004	<0.0004	0.0145	0.009	< 0.5	3.5	< 0.5	< 1.0
CEA 4-3 #33	<0.0004	<0.0004	0.0041	0.011	< 0.5	2.1	< 0.5	< 1.0
CEA 4-3 #34	<0.0004	<0.0004	0.0152	0.013	< 0.5	2.8	< 0.5	< 1.0
CEA 4-3 #35	<0.0004	<0.0004	0.0035	0.006	< 0.5	<=0.500	< 0.5	< 1.0
CEA 4-3 #36	<0.0004	<0.0004	<0.0004	0.002	< 0.5	0.9	< 0.5	< 1.0
CEA 4-3 #37	<0.0004	<0.0004	<0.0004	0.003	< 0.5	0.85	< 0.5	< 1.0
CEA 4-3 #38	<0.0004	<0.0004	<0.0004	0.002	< 0.5	0.79	< 0.5	< 1.0
CEA 4-3 #39	<0.0004	<0.0004	0.0165	0.007	< 0.5	3.1	< 0.5	< 1.0
CEA 4-3 #42	<0.0004	<0.0004	0.0026	0.007	11.7	70.9	< 0.5	416
CEA 4-3 #43	<0.0004	<0.0004	0.0024	0.011	14.0	45.2	< 0.5	291
CEA 4-3 #44	<0.0004	<0.0004	<0.0004	0.011	< 0.5	0.75	< 0.5	< 1.0
CEA 4-3 #45	<0.0004	<0.0004	0.0044	0.006	11.6	92.3	< 0.5	736
CEA 4-3 #46-1	<0.0004	<0.0004	0.0025	0.013	12.3	50.5	< 0.5	363
CEA 4-3 #46-2	<0.0004	<0.0004	0.0023	0.012	1.1	5.9	< 0.5	62.7
CEA 4-3 #46-3	<0.0004	<0.0004	0.0049	0.013	8.6	93.3	< 0.5	573
CEA 4-3 #47	<0.0004	<0.0004	0.0004	0.006	8.0	6.5	< 0.5	< 1.0
CEA 4-3 #48	<0.0004	<0.0004	0.0007	0.017	32.1	36.8	< 0.5	< 1.0
CEA 4-3 #49	<0.0004	<0.0004	<0.0004	0.007	10.5	8.5	< 0.5	< 1.0
CEA 4-3 #51	<0.200	<0.200	<0.200	2.29	< 0.5	1.2	< 0.5	< 1.0
CEA 4-3 #52	<0.200	<0.200	<0.200	2.38	< 0.5	1.1	< 0.5	< 1.0

Sample ID	Ag	Tl	V	Zn	Chlorate	Chloride	Chlorite	Per-chlorate
CEA 4-3 #53	<0.200	<0.200	<0.200	2.88	< 0.5	1.2	< 0.5	< 1.0
CEA 4-3 #55	<0.200	<0.200	<0.200	3.15	< 0.5	1.1	< 0.5	< 1.0
CEA 4-3 #56	<0.200	<0.200	<0.200	3.14	< 0.5	1.1	< 0.5	< 1.0
CEA 4-3 #57	<0.200	<0.200	<0.200	2.18	< 0.5	1.2	< 0.5	< 1.0

APPENDIX D: QUALITY ASSURANCE

Several standard QA/QC procedures were used in this study. Field sampling quality assurance was evaluated by collecting triplicate snow samples from within each impacted area for each test, and some of the samples were analytical duplicates, except for the cases where the entire impacted snow area was removed. In addition, the snow samples were analyzed by two different analytical laboratories (CRREL and EL) and CRREL analyzed these samples on two different occasions as well. The filter residue samples were analyzed by multiple laboratories (CRREL and EL) for the partial digestions. These results were then compared against a complete digestion of all residues for a sample which was performed by APPL Laboratories. Background multi-increment snow and soil samples also were collected in triplicate as a point of comparison. During the analyses initial calibration standards were run to assess the instrument's linear range. Samples were run several times to obtain an estimate of analytical precision. Also analyzed were calibration blanks, and inter element standards. A calibration blank and a continuing calibration verification (CCV) standard were run after every 10 samples. For each batch run a method blank, laboratory control sample, matrix spike, matrix duplicate, matrix spike duplicate, and known standard were prepared and analyzed. In addition, a reference soil standard NIST 2709 and 2710 were analyzed. Finally, representative snow and soil samples were sent to an independent third party laboratory, APPL Laboratories, for confirmation analysis.

The first assessment of results involved the collection of replicate (3x) multi-increment snow samples in the field and analysis by multiple laboratories (Tables D-1 and D-2). A decision unit was defined for each test and typically 100-increment samples were collected. A background area was defined as well and three replicate samples were collected from within the decision unit. Typically, the target relative standard deviation (RSD) for field replicate of soil samples is 30 percent. In this case, the RSD for the metals in the snow sample is > 30 percent. This includes the native metals and potential anthropogenic metals. This large error is believed to be the result of the very low concentrations of metal in the snow samples. The error is large for samples analyzed by CRREL (Table D-1) and by EL (Table D-2). In contrast, the soil samples collected using the multi-increment sampling approach generally yielded RSDs for the replicate samples < 30 percent (Table D-3). However, the concentration of metal in the soil samples was much higher as compared to the concentration in the snow samples. The only metals in soil exceeding the 30% RSD criteria were ones that were not anthropogenically introduced from the pyrotechnic test. It is possible that the metals in the soil, including the background location, have been previously influenced by other range activities. It is also possible that the native distribution of some metals is highly heterogeneous.

Table D-1. Evaluation of multi-increment filtered snow sample replication using percent Relative Standard Deviation (RSD) and analyzed by CRREL.

		Percent Relative Standard Deviation (RSD)							Mean (mg/L)						
Device Tested	Test Number	Al	Ba	Fe	K	Mg	Na	Sb	Al	Ba	Fe	K	Mg	Na	Sb
Background		34	NA	15	NA	8	29	NA	0.023	NA	0.013	0.123	0.080	0.986	0.013
M18	Test 1	69	**56**	**54**	**16**	**31**	24	NA	0.030	**0.270**	**0.008**	**17.7**	**4.59**	0.284	0.0003
M18	Test 2	17	**47**	**8**	**39**	**22**	25	82	0.025	**0.577**	**0.005**	**35.5**	**7.92**	0.647	0.002
M18	Test 3	47	**60**	**75**	**74**	**58**	20	53	0.019	**0.384**	**0.005**	**57.7**	**7.80**	1.03	0.012
M21	Test 1	**154**	**30**	25	**NA**	20	27	NA	**3.20**	**152**	0.002	**NA**	0.089	0.911	NA
M21	Test 2	**161**	**17**	NA	**22**	50	11	87	**12.0**	**327**	MA	**0.158**	0.183	1.10	0.0009
M21	Test 3	**27**	**8**	NA	**45**	39	31	122	**19.0**	**224**	0.009	**0.0192**	0.153	1.07	0.002
M127A1	Test 1 Near Flare	66	80	158	**68**	149	74	124	0.009	1.05	0.005	**11.1**	0.583	1150	0.003
M127A1	Test 1 10 downgradient	77	102	121	**77**	34	21	NA	0.048	0.040	0.003	**0.034**	2.79	1.25	NA
M127A1	Test 2 Near Flare	162	49	NA	**67**	125	51	NA	0.548	1.93	NA	**18.0**	0.056	1067	0.002
M127A1	Test 2 10 m downgradient	39	NA	18	**58**	27	18	58	0.015	NA	0.005	**0.124**	**2.01**	**1.96**	**0.001**
M117	Test 1	**7**	**NA**	NA	**46**	**16**	**17**	**13**	**0.0119**	**NA**	NA	**269**	**32.6**	**6.15**	**38.7**
M117	Test 2	**14**	**NA**	NA	**82**	**14**	**55**	**29**	**0.142**	**NA**	MA	**213**	**33.9**	**6.56**	**47.0**

Bold values are those metals introduced anthropogenically from the tested pyrotechnic device. Each test consists of 3 replicate samples.

NA = not analyzed

Table D-2. Evaluation of multi-increment filtered snow sample replication using percent Relative Standard Deviation (RSD) and analyzed by EL.

Device Tested	Test Number	Sb	As	Ba	Cr	Co	Cu	Pb	Mn	Mo	Ni	Se	V	Zn	Chlorate	Chloride	Perchlorate
Background		ND	ND	51	ND	ND	5	ND	6	ND	ND	ND	ND	5	ND	20	ND
M18	Test 1	38	ND	**57**	57	42	53	**10**	**25**	ND	88	16	ND	52	**54**	11	**ND**
M18	Test 2	26	ND	**39**	41	ND	13	**ND**	**60**	ND	49	0	ND	39	**66**	38	**ND**
M18	Test 6	14	ND	**45**	47	ND	27	**ND**	**15**	ND	71	ND	39	64	**79**	98	**ND**
M21	Test 1	13	ND	**30**	ND	ND	**ND**	**ND**	ND	ND	ND	ND	ND	**29**	**ND**	19	ND
M21	Test 2	19	ND	**5**	ND	ND	**ND**	**ND**	ND	ND	ND	ND	ND	**13**	**ND**	5	ND
M21	Test 3	13	ND	**11**	ND	ND	**ND**	**ND**	ND	ND	ND	ND	ND	**20**	**ND**	5	ND
M127A1	Test 1 Near Flare	**115**	ND	**75**	**89**	**ND**	105	**ND**	ND	**ND**	ND	47	120	**90**	ND	33	**ND**
M127A1	Test 1 10 m downgradient	**ND**	ND	**54**	**ND**	**ND**	37	**ND**	21	**ND**	ND	ND	ND	**25**	ND	4	**ND**
M127A1	Test 2 Near Flare	**ND**	ND	**44**	**69**	**ND**	150	**87**	ND	**ND**	ND	83	87	**37**	ND	20	**ND**
M127A1	Test 2 10m downgradient	**ND**	ND	**171**	**ND**	**ND**	95	**ND**	62	**ND**	ND	ND	ND	**66**	ND	83	**ND**
M117	Test 1	**88**	25	48	33	ND	80	ND	**82**	61	12	33	42	31	**13**	99	**61**
M117	Test 2	**32**	27	29	70	ND	27	7	**58**	ND	30	23	45	5	**78**	88	**77**

Highlighted and bold values are those metals introduced anthropgenically from the tested pyrotechnic device.
Each test consists of 3 replicate samples.
ND = non-detect so RSD could not be calculated.

Table D-3. Evaluation of multi-increment soil field replicate (3x) samples using percent Relative Standard Deviation (RSD).

Munition Type Tested	Test	Al	As	Ba	Be	Ca	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	P	Sb	V	Zn
Background		1	15	1	1	3	4	12	56	<1	3	1	2	6	7	2	9	1	2
M18 Smoke Grenade	Test 6	14	38	**17**	13	9	12	35	12	**10**	**15**	**10**	12	24	10	48	36	11	9
M 21 Arty Simulator	Test 1	1	11	**2**	2	1	1	2	**10**	1	1	1	2	2	2	13	2	1	**6**
M117 Booby Trap	Test 1	3	5	5	3	3	3	10	66	4	5	3	**5**	12	6	42	**5**	3	2
M127A1 Pop Flare	Test 1	2	2	**4**	2	5	**3**	**27**	6	<1	6	3	2	1	6	2	**13**	3	**4**
M127A1 Pop Flare	Test 2	2	13	**3**	1	4	**2**	**10**	2	1	4	2	5	8	6	2	**9**	2	**2**

Bold values are those metals introduced anthropgenically from the tested pyrotechnic device. Each test consists of 3 replicate samples.

The snow samples were analyzed by both the EL laboratory in Vicksburg, MS and the CRREL laboratory in Hanover, N.H. The analytical quality assurance measures practiced by the two laboratories are reviewed below. Following the general review of analytical quality assurance is a discussion of additional measures taken to assess data quality, which included a substantial number of samples analyzed by both laboratories as well as analyses of multiple portions of the solid residue on the filters.

Additional quality assurance measures were taken because the sample suite for these experiments was complex in that it contained water samples from melted snow, solid residue from filtering of the melted snow, and soil. The solid residue samples provided unusual matrices based on the original composition of the munition such that these varied from having only traces of an analyte to relatively high quantities in the subsample collected for analysis. Additionally, munitions such as these probably do not burn with 100% efficiency such that some of the original material is intact and some highly combusted.

ERDC (EL)

The EL provided standard data packages similar to those available from commercial laboratories. These data were evaluated with respect to the final use of the data but are not included in this report. For example, replicates were deemed satisfactory when either result would lead to the same conclusion regarding data interpretation. For a research and development project such as this one, there are no specific criteria. In this case, duplicates and spikes were considered satisfactory when agreement was demonstrated by a relative percent difference (RPD) of 10-25%. Results that were closer in agreement than 10% were deemed excellent. Near the detection limit, however, percentage differences could not be used. In those cases, the status of the agreement was based on reviewer judgment. Near the detection limit, the duplication could be as poor as 50% or more and still indicate a successful comparison.

Batch Report: 0051401

Blanks: Antimony (0.279 mg/L), barium (O.283 mg/L), and copper (0.181 mg/L) were reported in the blanks as well as smaller quantities of tin and zinc.

Laboratory Calibration Standards (LCS): All LCS results were acceptable, including for those elements found in blanks. The LCSs were all sufficiently close to expected values that data quality would not be harmed by the same percentage recovery for the investigation samples.

Duplicate: The snow duplicate samples had several RPD values greater than 25%: (Ba-36%, Cr-45.8%, Cu-38%, Pb-35.9%, and Mn-44.6%) for analytes of interest.

Matrix Spike: The percent recoveries on the spikes were all acceptable ranging from ~85-108%. Although recovery was acceptable, it should be noted that the antimony spike was unrealistically high, being an order of magnitude greater than the reported concentrations in the investigation samples.

Batch Report: 0040705

Blanks: Two blanks were analyzed with this data set, which contained the filter residue samples, and both had detectable levels of antimony, barium, copper, and zinc. In all cases except barium (~0.2-0.8 mg/kg) were near or below the reporting limits.

Laboratory Calibration Standards (LCS): There were two LCS samples and all results were acceptable. The LCSs were all close enough to expected values that data quality would not be harmed by the same level of recovery for the field samples.

Duplicates: RPDs on the duplicate samples were all less than 25% except for antimony and chromium which were 25-30%. Hence, these results are acceptable.

Matrix Spike: Recoveries were all acceptable. The antimony recovery was the poorest, being approximately 25% low.

Batch Report: 0040201

Blanks: A sample of milli-Q water was analyzed. Traces of antimony and barium were reported. Filtered milli-Q water was also analyzed. Traces of antimony, barium, copper, lead and zinc were reported. A sample preparation blank had traces of antimony and zinc. All of the detections in these blanks were near enough to the reporting limits, that data interpretation should not have been affected because the investigation samples had much higher quantities of the analytes.

Laboratory Calibration Standards (LCS): All LCS results were acceptable. The LCS was close enough to the expected value that data quality would not be harmed by the same level of recovery for the field samples.

Duplicate: The RPDs for antimony (>75%) and copper (>40%) were not acceptable, although the antimony results were slightly below the lab reporting limit; therefore, it is not necessary to flag antimony results. A second sample contained antimony at 50% more than the reporting limit and duplication for this sample was excellent as it was for all analytes. However, a third duplicate contained antimony at an order of magnitude more than the reporting limit and duplication was very poor (RPD=198%). In this case, the duplicate result was low. Copper also had poor results for this sample (RPD=142%).

Matrix Spike: Three matrix spikes were analyzed. The first had acceptable results for all analytes, although the barium result was outside the acceptable recovery range. The second matrix spike was acceptable for all analytes of interest. Finally, the third sample had acceptable results for all analytes.

Summary: The summary of the QA results is that data for all of the elements, except antimony associated with the filter residue samples were acceptable. There was greater variability in antimony results especially for the filter residue samples. The uncertainty associated with the antimony results is a function of the known poor recovery during digestion following the standard USEPA Method 3050B protocol

CRREL

Soil

Continuing calibration verification (CCV) was evaluated to determine whether the instrument was within acceptable calibration. In general, failure of the CCV indicates that the initial calibration is no longer valid and should trigger recalibration and the reanalysis of the associated samples in the analytical sequence. Five CCVs were run with the soil samples at a rate of approximately every ten with no failures of CCV noted.

Blanks: A digestion blank was run with no significant detections. Deionized water blanks had readings that were notable relative to the concentrations in the investigation samples for many of the analytes. For example, the blank contained nearly 50% of the maximum reported value for the test samples for Ba-~55%, Pb-~40% and Sb-~50%. Typically, blanks this high in relation to the investigation samples impart a very high level of uncertainty in the final results. Typically with blanks this high the blank values are subtracted from the measured sample value. However, this was not done in this case since the two blanks showed excellent reproducibility with RPDs for all lines measured, that is, <10% and most <3%.

Solution Standards: A series of 2 ppb standards were analyzed. The lead result was low by approximately 27 percent. All other metals were within 10% of the expected value.

Summary: Precision for these data appears acceptable based on the replicate sample results presented in Appendix E, Table E-1 .

Snow and Filter

There were four blanks designated BLK1-4. Results for these were only a few percent or less of samples having significant reported values.

EL and CRREL Comparisons

As noted in the introduction to this Appendix, the sample suite for these experiments was complex. Furthermore, the EL and CRREL laboratories did not use identical analytical procedures, although they were functionally similar. Both laboratories used block digesters for the solid residues and both used ICP for the analysis. However, EL used only HNO_3 for digestion whereas CRREL used a HNO_3/HCl mixture and El used ICP-MS and CRREL used ICP-OES for the final analysis. Hence, most samples were analyzed by both laboratories and some samples were analyzed multiple times at CRREL to ensure that data quality was adequately understood. The following comparisons were performed using reviewer judgment because the small and/or uneven number of replicates precluded the use of rigorous statistical methods. Moreover, such a review was not deemed necessary considering that, as the main text has shown, metal recoveries were, in general, quite low.

Snow Samples: EL versus CRREL analytical values were not seriously different for the water (snow) samples (Table D-6). For example, the following pairs (Table D-4) illustrate the comparison for barium (mg/L) for the M127A1 signal illumination ground white star parachute.

Table D-4. Evaluation of snow sample barium concentrations (mg/L) between samples analyzed at EL and CRREL.

Sample ID	EL	CRREL
CEA-4-3 #26	0.654	0.524
CEA-4-3 #27	2.27	2.02
CEA-4-3 #30	0.096	0.110
CEA-4-3 #32	2.90	2.56
CEA-4-3 #39	4.45	4.05

- Barium snow data are comparable as are the filter residue data for EL with the exception of sample CEA 4-3-1AF Rep 1which had two filters, A and B. CRREL reported 229 and 46.4 mg/L for barium on these respectively (Table D-5). EL reported 89.2 and 57.9 mg/L, respectively (Table D-5). The barium results for replicates of CEA4-3-1AF were in good agreement. The reported result for sample CE4-3-21F by EL was 57,700 mg/kg barium. In comparison, the CRREL reported result was 36,700 mg/kg. The inherent heterogeneity of the sample and sample handling differences could explain these results.

- Antimony snow sample results are in good agreement between CRREL and EL, with the exception being samples CEA4-3-1AF Rep. 1, CEA4-3-4F, CEA4-3-42F, and CEA4-3-47F (Table D-5). The most serious difference was the result for sample CEA 4-3-42F where EL reported a value of 71,200,000 mg/kg (Table D-5). Upon checking with EL, it was acknowledged that this very high value was in error. The sample was not rerun by EL.

- Lead in snow samples analyzed by CRREL was reported as non-detect. Where both labs have filter residue sample results they are in good agreement, with the exception of sample CEA4-3-1AF Rep. 1. EL reported a value of 2.4 mg/kg and CRREL a value o f 144 mg/kg (Table D-5)

- Manganese was not analyzed for by CRREL in the snow samples. The EL filter residue values are in agreement with CRREL results, except for sample CEA4-3-1AF Rep. 1where EL reported a value of 28.1 mg/kg and CRREL 228 mg/kg.

- Copper in snow samples analyzed by CRREL was reported as non-detect. Again, the only appreciable difference in results for the filter residue samples was associated with sample CEA4-3-1AF Rep. 1 (Table D-5).

- Zinc in snow samples analyzed by CRREL was reported as non-detect with no differences noted for the filter residue samples.

The conclusion of this review was that the CRREL data would be used for two reasons. First, samples are housed at CRREL and re-analysis is relatively easy and differences with EL with respect to calculating total metal recovery were not significant. Second, EL appeared to have more difficulty with blanks both analytically and with their analysis of the background sample. Although some

snow sample filter residue sample digestates exhibited precipitates upon return from EL to CRREL it is not believed these had a bearing since differences with EL with respect to calculating total metal recovery were not significant. There does appear to be an issue with the EL result for filter residue sample CEA4-3-1AF Rep. 1, which had substantially lower metal levels of antimony, barium, copper, lead, and manganese as compared to the CRREL result.

Table D-5. Comparison of filter residue results (mg/kg) by laboratory and calculated percent Relative Standard Deviation (RSD).

Sample ID	Device Tested	Digested/ Analyzed	Date Analyzed	Al	Sb	As	Ba	Be	Cd	Ca	Cr	Co	Cu	Fe	Pb	Mn	Mg	Mo	Ni	K	Se	Ag	Na	Tl	Sn	V	Zinc
EA4-3-1AF	M18	EL/EL	5/7/10	NA	0.30	0.40	89.2	ND	ND	NA	21.7	0.9	3.1	NA	2.4	28.1	NA	ND	43.8	NA	ND	ND	NA	ND	5.7	1.4	22.4
Rep 1		EL/CRREL	6/1/10	1810	72.1	44.5	229	42.6	50.1	1,280	99.4	83.4	86.4	2,760	81.6	228	1,210	NA	144	963	46.0	26.9	872	36.3	NA	85.6	209
		EL/CRREL	9/8/10	1710	64.1	38.6	225	41.0	60.0	1,310	99.1	87.9	83.6	2,960	83.2	210	1,200	NA	138	830	40.3	33.3	744	45.8	NA	78.0	2,089
		% RSD		**34**	**1**	**1**	**4**	**1**	**1**	**26**	**2**	**2**	**2**	**58**	**2**	**4**	**24**	**0**	**3**	**16**	**1**	**1**	**15**	**1**	**NC**	**2**	**4**
CEA4-3-1AF	M18	EL/CRREL	6/1/10	1820	72.3	45.1	254	43.3	50.6	1,290	100	84.2	87.3	2,790	81.8	228	1210	NA	146	968	45.9	26.9	859	36.8	NA	86.1	211
Rep 2		EL/CRREL	9/8/10	1720	64.5	38.7	224	40.6	60.1	1,290	98.8	88.1	83.4	2,930	83.7	209	1190	NA	138	826	40.6	31.5	742	45.6	NA	78.3	209
		% RPD		**34**	**1.3**	**1**	**4**	**1**	**1**	**<1**	**2**	**2**	**2**	**58**	**2**	**4**	**24**	**NC**	**3**	**16**	**1**	**1**	**15**	**1**	**NC**	**2**	**4**
CEA4-3-1AF	M18	EL/CRREL	6/1/10	1020	0.40	1.1	68.9	0.1	ND	487	10.8	ND	ND	2,270	ND	21.2	463	NA	43.1	211	ND	ND	90.4	ND	NA	1.7	17.6
Rep 3		EL/CRREL	9/8/10	982	0.30	0.50	77.6	ND	ND	500	21.7	1.4	6.5	2430	3.1	31.4	466	NA	49.9	191	NA	NA	66.0	NA	NA	1.5	28.8
		% RPD		**19**	**<1**	**<1**	**2**	**NC**	**NC**	**10**	**<1**	**NC**	**NC**	**48**	**NC**	**1**	**9**	**NC**	**1**	**4**	**NC**	**NC**	**1**	**NC**	**NC**	**<1**	**<1**
CEA 4–3-1BF	M18	EL/EL		NA	0.10	ND	57.9	ND	ND	NA	14.3	ND	0.5	NA	0.4	2.1	NA	ND	33.9	NA	ND	ND	NA	ND	4.5	0.1	3.8
Rep 1		EL/CRREL	6/1/10	79.7	0.20	0.20	46.4	0.0	ND	72.2	5.0	ND	ND	181	ND	ND	169	NA	29.0	98.9	0.2	ND	80.3	ND	NA	0.1	ND
		EL/CRREL	9/8/10	76.4	0.10	0.10	51.5	ND	ND	72.8	13.4	ND	2.9	192	0.6	2.1	166	NA	34.1	89.7	0.0	NA	35.0	0.1	NA	0.0	5.1
		% RSD		**1**	**0**	**<1**	**1**	**NC**	**NC**	**1**	**NC**	**NC**	**<1**	**3**	**<1**	**<1**	**2**	**NC**	**<1**	**1**	**<1**	**NC**	**1**	**NC**	**NC**	**<1**	**<1**
CEA4-3-4F	M18	EL/EL		NA	0.20	0.40	5570	ND	0.7	NA	888	0.8	3.4	NA	30.4	39.6	NA	0.2	3,050	NA	0.3	3.5	NA	ND	18.6	1.3	368
		EL/CRREL	6/1/10	784	5.5	ND	4580	0.1	ND	1,180	873	ND	ND	1,610	20.9	33.4	13,100	NA	3,280	512	ND	ND	132	ND	NA	0.6	448
		EL/CRREL	9/8/10	752	5.9	ND	4100	0.0	ND	1,170	771	2.5	6.5	1,690	30.9	41.5	12,800	ND	2,860	443	NA	NA	64.6	NA	NA	0.5	436
		% RSD		**1**	**<1**	**NC**	**5**	**<1**	**NC**	**1**	**1**	**<1**	**<1**	**2**	**<1**	**<1**	**15**	**NC**	**3.4**	**<1**	**NC**	**NC**	**0.1**	**NC**	**NC**	**<1**	**<1**
CEA4-3-9F	Bckd	EL/EL		NA	0.2	0.20	42.2	ND	ND	NA	0.9	0.3	2.1	NA	1.3	13.6	NA	ND	1.2	NA	ND	ND	NA	ND	4.8	0.8	29.4
		EL/CRREL	6/1/10	484	0.0	0.10	22.0	0.0	ND	566	ND	ND	ND	799	ND	ND	275	NA	ND	93.4	ND	ND	174	ND	NA	0.8	21.3
		EL/CRREL	9/8/10	459	ND	ND	35.6	ND	ND	576	0.9	0.1	5.1	847	1.6	13.7	275	NA	1.0	85.6	NA	NA	103	ND	NA	0.7	33.5

Sample ID	Device Tested	Digested/ Analyzed	Date Analyzed	Al	Sb	As	Ba	Be	Cd	Ca	Cr	Co	Cu	Fe	Pb	Mn	Mg	Mo	Ni	K	Se	Ag	Na	Tl	Sn	V	Zinc
		% RSD		1.2	NC	NC	<1	NC	NC	2	<1	<1	<1	2	<1	<1	1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
CEA4-3-12F	M21	EL/EL		NA	1.2	0.5	57,700	ND	0.2	NA	3.4	0.7	13,000	NA	282	23.6	NA	0.4	10.9	NA	1.0	0.3	NA	ND	23.8	17.4	56.0
		EL/CRREL	6/1/10	147,000	1.4	2.9	36,700	0.1	ND	1,010	ND	ND	11,400	1,200	274	4.9	362	NA	ND	63.0	ND	ND	169	ND	NA	15.7	32.6
		EL/CRREL	9/8/10	141,000	0.8	2.5	30,500	ND	ND	1,000	2.6	ND	9,650	1,200	242	18.6	346	NA	8.6	57.1	NA	NA	76.5	ND	NA	14.4	45.7
		% RPD		239	<1	<1	52	NC	NC	2	<1	NC	16	<1	<1	<1	1	NC	<1	<1	NC	NC	<1	NC	NC	<1	<1
CEA4-3-26F	M127A1	EL/EL		NA	0.2	ND	125	ND	ND	NA	1.0	2.2	1.1	NA	0.2	38.8	NA	ND	4.4	NA	ND	ND	NA	ND	3.0	2.5	10.5
		EL/CRREL	6/1/10	4,900	0.3	0.4	112	0.1	ND	242	ND	ND	ND	900	ND	31.6	296,000	NA	ND	1,790	ND	ND	1300	ND	NA	2.7	2.1
		EL/CRREL	9/8/10	4,510	0.2	0.4	108	ND	ND	249	0.8	2.3	3.0	952	3.3	37.9	289,000	ND	4.3	1,500	ND	ND	966	ND	ND	2.4	12.0
		% RSD		26	<1	<1	<1	NC	NC	1	<1	<1	<1	5	<1	<1	1648	NC	<1	9	NC	NC	6	NC	NC	<1	<1
CEA4-3-29F	M127A1	EL/EL		NA	0.3	0.1	400	ND	ND	NA	0.4	ND	0.6	NA	0.4	3.2	NA	ND	0.4	NA	ND	ND	NA	ND	4.8	0.2	248
		EL/CRREL	6/1/10	298	0.4	ND	335	0.0	ND	226	ND	ND	ND	265	ND	ND	3790	NA	ND	267	ND	ND	759	ND	NA	0.2	323
		EL/CRREL	9/8/10	282	0.3	ND	322	ND	ND	234	0.4	ND	5.0	279	0.2	3.6	3730	ND	0.3	227	ND	ND	568	ND	ND	0.1	318
		% RSD		<1	<1	NC	1	NC	NC	1	<1	NC	<1	1	<1	<1	10	NC	<1	1	NC	NC	2	NC	NC	<1	1
CEA4-3-33F	M127A1	EL/EL		NA	0.2	ND	187	ND	ND	NA	0.9	1.9	0.8	NA	0.2	24.8	NA	ND	3.5	NA	ND	ND	NA	ND	2.8	2.8	1.9
		EL/CRREL	6/1/10	6,100	0.2	0.5	161	0.1	ND	354	ND	ND	ND	1,230	ND	23.5	236,000	NA	ND	2,810	ND	ND	1370	ND	NA	3.5	ND
		EL/CRREL	9/8/10	5,790	0.3	ND	158	ND	ND	359	0.8	2.3	3.2	1,310	4.5	31.4	231,000	ND	3.9	2,400	ND	ND	1110	ND	ND	3.2	2.0
		% RSD		61	0.0	NC	2	NC	NC	3.8	<1	<1	<1	14	<1	<1	2440	NC	<1	25	NC	NC	12	NC	NC	<1	<1
CEA4-3-42F	M117	EL/EL		NA	71,200,000*	6.5	38.6	ND	ND	NA	6.0	ND	17.1	NA	0.4	92.9	NA	ND	3.5	NA	ND	ND	NA	0.1	0.2	0.3	66.7
		EL/CRREL	6/1/10	393	2370	8.0	24.4	0.1	ND	1,200	ND	ND	15.4	87.2	ND	97.2	73,800	NA	ND	889	ND	ND	141	ND	NA	0.3	83.3
		EL/CRREL	9/8/10	373	2082	6.8	31.8	ND	ND	1,220	6.3	ND	22.1	93.1	ND	93.1	71,700	ND	3.8	756	ND	ND	58.2	0.2	ND	0.2	89.1
		% RSD		33	184	1	3	NC	NC	109	1	NC	2	8	NC	8	6350	NC	<1	67	NC	NC	5	<1	NC	<1	8
CEA4-3-47F	M18	EL/EL		NA	3.6	0.3	13800	ND	2.2	NA	2130	0.4	5.3	NA	68.2	84.3	NA	0.4	6810	NA	0.8	12.0	NA	ND	40.0	0.9	628.0

Sample ID	Device Tested	Digested/ Analyzed	Date Analyzed	Al	Sb	As	Ba	Be	Cd	Ca	Cr	Co	Cu	Fe	Pb	Mn	Mg	Mo	Ni	K	Se	Ag	Na	Tl	Sn	V	Zinc
		EL/CRREL	6/1/10	569	16.9	ND	12,200	0.0	ND	3160	2130	ND	ND	785	ND	ND	22,700	NA	7,920	766	ND	ND	865	ND	NA	ND	723
		EL/CRREL	9/8/10	539	16.7	ND	11,000	ND	ND	3250	1950	1.4	40.8	818	55.0	102	22,400	ND	7,063	683	ND	ND	430	ND	NA	ND	785
		% RSD		**<1**	**<1**	**NC**	**4**	**NC**	**NC**	**1**	**1**	**<1**	**<1**	**<1**	**<1**	**<1**	**9**	**NC**	**3**	**<1**	**NC**	**NC**	**<1**	**NC**	**NC**	**NC**	**<1**
CEA4-3-51F	M21	EL/EL	5/7/10	NA	2.0	0.3	7,230	ND	0.1	NA	3.0	0.6	13,700	NA	388	21.1	NA	0.2	13.1	NA	0.1	0.4	NA	ND	28.7	17.3	39.1
		EL/CRREL	6/1/10	115,000	2.2	2.4	5,160	0.2	ND	703	ND	ND	11,400	834	279	6.3	292	NA	ND	45.3	ND	ND	116	ND	NA	15.4	26.9
		EL/CRREL	9/8/10	110,000	1.7	1.5	3,640	ND	ND	693	2.2	ND	9,720	867	241	17.5	282	ND	10.5	46.5	ND	ND	72.3	ND	NA	14.0	37.3
		% RSD		**441**	**<1**	**<1**	**15**	**NC**	**NC**	**3**	**<1**	**NC**	**39**	**4**	**1**	**<1**	**1**	**NC**	**<1**	**<1**	**NC**	**NC**	**<1**	**NC**	**NC**	**<1**	**<1**

Bckd = background, NA = not analyzed, NC = RSD not calculated, ND = not detected

*indicates analytical error

Table D-6. Comparison of calculated metal mass results (mg) for snow samples by laboratory.

Sample ID	Laboratory	Al	Sb	As	Ba	Be	Ca	Cr	Co	Cu	Fe	Pb	Mn	Mg	Mo	Ni	K	Se	Na	V	Zn
Background																					
CEA4-3-9	EL	NA	ND	ND	0.07	ND	NA	ND	ND	0.001	NA	0.001	0.02	NA	ND	0.001	NA	ND	NA	ND	0.02
	CRREL	0.03	ND	ND	ND	ND	2.2	ND	ND	ND	0.02	ND	ND	0.15	NA	ND	ND	ND	1.6	ND	ND
CEA4-3-10	EL	NA	ND	ND	0.03	ND	NA	ND	ND	0.001	NA	ND	0.02	NA	ND	ND	NA	ND	NA	ND	0.02
	CRREL	0.03	ND	ND	ND	ND	2.1	ND	ND	ND	0.03	ND	ND	0.15	NA	ND	ND	ND	1.8	ND	ND
CEA4-3-11	EL	NA	ND	ND	0.07	ND	NA	ND	ND	0.002	NA	ND	0.03	NA	ND	ND	NA	0.002	NA	ND	0.04
	CRREL	0.03	ND	ND	ND	ND	3.5	ND	ND	ND	0.05	ND	ND	0.32	NA	ND	ND	ND	1.8	ND	ND
CEA4-3-44	EL	NA	0.07	ND	0.12	ND	NA	ND	ND	0.005	NA	ND	0.01	NA	ND	ND	NA	ND	NA	ND	0.03
	CRREL	0.11	0.03	ND	ND	ND	0.72	ND	ND	ND	0.02	ND	ND	0.09	NA	ND	0.30	ND	3.3	ND	ND
M18																					
Test 1 avg	EL	NA	0.02	ND	4.8	ND	NA	0.22	0.01	0.02	NA	0.01	0.83	NA	ND	0.20	NA	0.01	NA	ND	0.71
	CRREL	0.41	ND	0.01	3.7	ND	11.8	ND	ND	ND	0.11	ND	ND	62	NA	ND	237	0.01	3.8	ND	ND
Test 2 avg	EL	NA	0.02	ND	2.0	ND	NA	0.171	ND	0.003	NA	0.001	0.04	NA	ND	0.03	NA	0.002	NA	ND	0.03
	CRREL	0.09	0.01	0.00	1.7	ND	3.6	ND	ND	ND	0.01	ND	ND	27	NA	ND	113	ND	2.2	ND	ND
Test 3 avg	EL	NA	0.02	ND	0.46	ND	NA	0.039	ND	0.003	NA	0.000	0.005	NA	ND	0.08	NA	ND	NA	ND	0.01
	CRREL	0.02	0.01	ND	0.38	ND	0.97	ND	ND	ND	0.01	ND	ND	7.7	NA	ND	54.2	ND	1.1	ND	ND
M21																					
Test 1 avg	EL	NA	0.36	ND	229	ND	NA	ND	ND	ND	NA	ND	ND	NA	ND	ND	NA	ND	NA	ND	4.3
	CRREL	5.0	ND	ND	219	ND	1.7	ND	ND	ND	0.00	ND	ND	0.13	NA	ND	ND	ND	1.3	ND	ND
Test 2 avg	EL	NA	1.1	ND	825	ND	NA	ND	ND	ND	NA	ND	ND	NA	ND	ND	NA	ND	NA	ND	6.6
	CRREL	23	ND	ND	811	ND	2.7	ND	ND	ND	ND	ND	ND	0.50	NA	ND	0.42	ND	2.8	ND	ND
Test 3 avg	EL	NA	0.91	ND	697	ND	NA	ND	ND	0.69	NA	ND	ND	NA	ND	ND	NA	ND	NA	ND	7.9
	CRREL	53	0.01	ND	646	ND	3.6	ND	ND	ND	ND	ND	ND	0.48	NA	ND	0.59	ND	3.3	ND	ND

Sample ID	Laboratory	Al	Sb	As	Ba	Be	Ca	Cr	Co	Cu	Fe	Pb	Mn	Mg	Mo	Ni	K	Se	Na	V	Zn
M117																					
Test 1 avg	EL	NA	417	0.91	0.90	ND	NA	0.08	ND	0.06	NA	0.01	0.11	NA	0.00	0.03	NA	0.06	NA	0.03	0.11
	CRREL	1.5	463	1.016	ND	0.00	40	ND	ND	ND	ND	ND	ND	424	NA	ND	2791	0.05	82	0.01	ND
Test 2 avg	EL	NA	298	0.63	0.59	ND	NA	0.06	ND	0.03	NA	0.01	0.11	NA	0.00	0.02	NA	0.04	NA	0.02	0.11
	CRREL	1.1	335	0.72	ND	0.00	34	ND	ND	ND	ND	ND	ND	310	NA	ND	1778	0.02	71	0.01	ND
M127A1																					
Test 1 Avg	EL	NA	ND	ND	1.0	ND	NA	0.01	ND	0.00	NA	ND	ND	NA	ND	ND	NA	0.00	NA	ND	ND
	CRREL	0.01	ND	0.01	0.88	ND	0.59	ND	ND	ND	0.01	ND	ND	0.74	NA	ND	9.7	0.01	990	ND	ND
Test 2 Avg	EL	NA	ND	ND	0.07	ND	NA	ND	ND	ND	NA	ND	ND	NA	ND	ND	NA	ND	NA	ND	0.00
	CRREL	0.04	ND	ND	0.03	ND	0.22	ND	ND	ND	0.003	ND	ND	2.3	NA	ND	0.03	0.00	1.1	ND	ND
Test 4 Avg	EL	NA	ND	ND	0.04	ND	NA	ND	ND	0.001	NA	ND	0.00	NA	ND	ND	NA	ND	NA	ND	0.00
	CRREL	0.02	ND	ND	ND	ND	0.29	ND	ND	ND	0.006	ND	ND	2.0	NA	ND	0.12	ND	2.0	ND	ND
Test 5 Avg	EL	NA	ND	0.01	15	ND	NA	ND	ND	ND	NA	ND	ND	NA	0	ND	NA	0.01	NA	0.07	0.04
	CRREL	0.64	0.001	0.117	14	ND	4	ND	ND	ND	ND	ND	ND	ND	NA	ND	133	0.20	8304	0.06	ND

Table D-7 compares the results of a triplicate digestions of 0.5 or 1 gram of filter. The data demonstrate the difficulties in selecting appropriate methods for these samples. The chromium comparisons for the average are excellent, but the RSD for one of the sets of triplicate is poor. Copper has the best RSD results, but one value is approximately twice the other. It is not possible to ascertain whether the variations are a consequence of sample heterogeneity or problems occurring during digestion/analysis. For this reason, filter residue samples consisted of digestion of 5-g of material and these were prepared by collecting 20 increments from each sample.

Table D-7. CRREL results for triplicate analyses of two portions of filter sample CEA-4-3#1-BF.

Element	Weight grams	Average mg/kg	RSD (%)
Barium	0.5/1	401/400	33/19
Chromium	0.5/1	39.5/39.2	60/22
Copper	0.5/1	10.9/5.8	4/4
Iron	0.5/1	253/206	25/20
Potassium	0.5/1	331/363	22/18
Magnesium	0.5/1	159/184	25/27
Manganese	0.5/1	14.8/15.5	24/23
Sodium	0.5/1	11.2/9.4	15/17
Zinc	0.5/1	50.6/50.6	17/7

Finally, a comparison was made between the sub sampled filter residue and wholesale digestion of the entire filter residue mass after removing the subsample portion, 5g. Since the entire solid residue mass on the filter was generally over 50 g and in many instances well above 100g the removal of a small portion of the mass should have little impact on the entire sample digestions. The complete filter residue digestion performed by APPL Laboratories followed USEPA Method 3050B with the only difference being the mass of sample digested. Table D-8 suggests little difference between the partial residue digestions and the complete residue digestions. The sample calculations presented in Section 4 were determined the residue mass of the metal solid residue using the partial residue digestions analyzed by CRREL.

Table D-8. Comparison of metal mass (mg) calculation results for partial solid residue digestions and complete solid residue digestions.

Lab	Sample ID	Al	As	Ba	B	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Mo	Na	Ni	Pb	Sb	V	Zn
CRREL	1-BF	365	ND	290	NA	170	ND	ND	42	ND	813	269	432	11	NA	211	109	ND	ND	ND	242
APPL	1-BF	470	ND	473	140	NA	0.3	0	50	1.3	911	407	563	15	ND	NA	115	2.2	NA	0.8	229
CRREL	3F	400	ND	419	NA	304	ND	ND	18	ND	599	403	429	10	NA	594	47	ND	ND	ND	361
APPL	3F	556	ND	594	414	NA	ND	1.2	23	1.5	736	652	593	15	ND	NA	54	2.0	NA	0.7	411
CRREL	6F	2,009	ND	3,553	NA	2,046	ND	ND	282	ND	2,288	1,875	3,468	51	NA	4,144	1,033	ND	ND	ND	2,678
APPL	6F	2,800	1.8	7,310	4,310	NA	2.8	0.3	374	4.4	2,900	3,110	1,300	80	ND	NA	1,630	16	NA	2.9	3,950
CRREL	26F	4,091	ND	1,988	NA	714	ND	4.8	1.7	1.7	1,210	2,148	322,217	44	NA	3,966	4.7	ND	ND	2.8	1,592
APPL	26F	4,240	0.5	2,400	1,700	NA	0.2	5.2	1.8	1.3	1,330	2,490	345,000	50	ND	NA	4.4	0.4	NA	3.4	1,630
CRREL	28F	6,550	ND	1,519	NA	641	ND	4.6	1.5	1.6	1,739	2,847	332,411	41	NA	3,558	4.6	ND	ND	4.8	1,277
APPL	28F	6,790	ND	1,850	1,390	NA	ND	4.8	1.5	1.1	1,800	3,220	323,000	45	ND	NA	4.0	0.3	NA	5.4	1,280
CRREL	32F	13,442	ND	1,181	NA	878	ND	7.1	1.7	5.7	3,234	5,553	294,447	34	NA	5,369	3.9	ND	ND	11	920
APPL	32F	13,800	ND	1,450	925	NA	ND	7.0	1.8	4.0	3,240	6,180	287,000	37	ND	NA	3.4	0.8	NA	12	833
CRREL	35F	5,019	ND	1,154	NA	487	ND	4.1	1.4	1.4	1,458	2,417	337,196	45	NA	2,780	ND	ND	ND	3.9	814
APPL	35F	5,560	ND	1,390	764	NA	ND	4.3	1.4	1.0	1,500	2,790	360,000	49	ND	NA	4.4	0.2	NA	4.5	716
CRREL	39F	11,590	ND	1,083	NA	678	ND	7.7	1.4	2.1	2,543	4,509	327,247	33	NA	4,022	3.7	ND	ND	8.9	522
APPL	39F	11,800	ND	1,340	491	NA	ND	7.7	1.4	1.6	2,600	5,230	326,000	37	ND	NA	3.3	0.2	NA	10	451
CRREL	29F	10,942	ND	17,077	NA	5,528	ND	ND	9	ND	298	9,192	9,776	5.6	NA	24,840	ND	ND	ND	ND	15,321
APPL	29F	11,300	3.9	18,700	14,400	NA	0.5	0.2	10	5.9	389	11,200	9,430	9.4	ND	NA	1.9	2.6	NA	1.0	14,100
CRREL	42F	1,629	20	491	NA	5,893	ND	ND	8.6	43	691	2,672	42,315	74	NA	2,326	ND	28	40,482	0.7	1,401
APPL	42F	1,460	17	583	1,280	NA	0.4	0.4	8.4	35	683	3,030	43,800	82	ND	NA	4.3	28	NA	0.9	1,350
CRREL	45F	1,217	26	276	NA	7,490	ND	ND	8.2	40	827	1,810	56,185	77	NA	593	ND	29	42,021	1.3	470
APPL	45F	1,090	24	345	316	NA	0.3	0.5	7.9	34	820	2,040	54,600	84	0.3	NA	4.7	30	NA	1.4	441

Lab	Sample ID	Al	As	Ba	B	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Mo	Na	Ni	Pb	Sb	V	Zn
CRREL	46-1F	1,018	12	497	NA	5,056	ND	ND	7.1	31	521	2,154	33,915	61	NA	1,320	ND	21	32,158	0.7	800
APPL	46-1F	982	11	599	714	NA	0.3	0.3	7.2	28	536	2,410	32,700	69	ND	NA	2.6	22	NA	0.9	764
CRREL	46-2F	935	17	386	NA	6,006	ND	ND	8	36	591	765	38,262	62	NA	746	ND	21	32,535	0.8	544
APPL	46-2F	871	16	470	419	NA	0.3	0.4	7.7	31	592	893	37,300	69	ND	NA	3.1	22	NA	0.9	528
CRREL	47F	9,122	ND	16,913	NA	5,114	ND	ND	620	ND	605	8,076	6,849	34	NA	19,773	2,201	ND	ND	ND	12,488
APPL	47F	9,380	3.3	19,000	11,800	NA	6.0	0.3	600	3.8	663	9,900	6,790	40	ND	NA	1,950	19	NA	1.3	11,400
CRREL	51F	122,331	ND	250	NA	1,328	ND	ND	2.9	9,531	883	337	320	22	NA	1,049	10	192	ND	15	598
APPL	51F	137,000	0.4	288	530	NA	0.3	0.6	3.2	11,600	959	440	347	26	0.1	NA	10	203	NA	17	505
CRREL	53F	150,671	ND	423	NA	1,879	ND	2.0	5.1	11,527	5,432	211	905	75	NA	611	14	167	ND	17	404
APPL	53F	158,000	0.8	517	313	NA	0.2	1.8	5.7	12,600	5,070	274	949	92	0.2	NA	15	184	NA	21	356
CRREL	55F	97,691	ND	774	NA	1,979	ND	ND	2.4	8,418	628	707	330	13	NA	2,131	7.5	132	ND	10	1,275
APPL	55F	115,000	0.5	901	1,190	NA	0.2	0.4	2.6	9,160	685	893	340	17	ND	NA	7.4	138	NA	11	1,150
CRREL	57F	66,554	ND	242	NA	2,769	ND	0.9	3.3	6,000	1,515	319	584	39	NA	837	7.2	67	ND	7.8	474
APPL	57F	78,100	0.6	290	449	NA	ND	0.8	3.5	6,060	1,590	399	589	46	0.1	NA	7.2	72	NA	9.0	425
CRREL	4F	4,765	ND	10,272	NA	3,500	ND	ND	875	ND	3,137	4,393	11,618	58	NA	8,882	3,611	29	ND	ND	5,846
APPL	4F	4,630	2.3	11,900	5,130	NA	6.8	0.8	814	5.9	2,850	5,240	11,000	65	ND	NA	3,480	27	NA	3.1	5,250
CRREL	9F	7,428	ND	10,309	NA	4,665	ND	ND	7	ND	2,572	5,838	1,261	35	NA	15,553	ND	ND	ND	ND	9,592
APPL	9F	7,840	3.4	11,400	8,820	NA	0.3	1.2	8.1	6.4	2,490	7,220	4,620	44	ND	NA	3.2	5.7	NA	3.1	8,630
CRREL	12F	97,181	ND	22,169	NA	2,020	ND	ND	4	8,635	1,170	1,565	499	17	NA	4,652	8.0	170	ND	12	2,701
APPL	12F	123,000	1.5	27,100	2,620	NA	0.2	0.6	4.8	8,900	1,200	1,960	527	21	ND	NA	7.9	173	NA	14	2,510
CRREL	14F	120,413	ND	18,226	NA	2,061	ND	ND	4	8,889	1,168	2,115	564	19	NA	6,142	8.6	157	ND	13	3,669
APPL	14F	129,000	1.5	22,600	3,470	NA	0.5	0.6	4.9	9,090	1,190	2,640	593	24	ND	NA	8.5	160	NA	15	3,350

APPENDIX E: SOIL RESULTS

Table E-1. Metal results (mg/kg) for surface soil samples.

Sample ID	Range	Number Increments	Weight < 2mm (g)	Weight > 2mm (g)	Rep	Comments	Munition Type Tested
1	74	50	469.9	162.9	1	Corresponds to snow samples CEA4-3 # 33, 34, 35	M127A1 Pop Flare
2	74	50	552.1	143.7	2	Corresponds to snow samples CEA4-3 # 33, 34, 35	M127A1 Pop Flare
3	74	50	529.5	106.4	3	Corresponds to snow samples CEA4-3 # 33, 34, 35	M127A1 Pop Flare
4	74	50	492.1	246.8	1	Corresponds to snow samples CEA4-3 # 36, 37, 38	M127A1 Pop Flare
5	74	50	448.6	230.2	2	Corresponds to snow samples CEA4-3 # 36, 37, 38	M127A1 Pop Flare
6	74	50	391.6	182.5	3	Corresponds to snow samples CEA4-3 # 36, 37, 38	M127A1 Pop Flare
7	4-1	100	1207.5	136.3	1	Corresponds to snow samples CEA4-3 # 12, 13, 14	M 21 Arty Sim
8	4-1	105	1182.2	123.4	2	Corresponds to snow samples CEA4-3 # 12, 13, 14	M 21 Arty Sim
9	4-1	100	1141.7	142.5	3	Corresponds to snow samples CEA4-3 # 12, 13, 14	M 21 Arty Sim
10	4-1	125	1552.3	78.9	1	Corresponds to snow samples CEA4-3 # 42, 43, 44	M117 Booby Trap
11	4-1	100	996.8	44.4	2	Corresponds to snow samples CEA4-3 # 42, 43, 44	M117 Booby Trap
12	4-1	100	874.8	62.8	3	Corresponds to snow samples CEA4-3 # 42, 43, 44	M117 Booby Trap
13	4-1	50	453.7	108.2	1	Corresponds to snow samples CEA4-3 # 9, 10, 11	Background
14	4-1	50	352.5	60.7	2	Corresponds to snow samples CEA4-3 # 9, 10, 11	Background
15	4-1	50	383.5	64.0	3	Corresponds to snow samples CEA4-3 # 9, 10, 11	Background
16	4-1	50	496.3	59.8	1	Corresponds to snow samples CEA4-3 # 47, 48, 49	M18 Smoke Grenade
17	4-1	50	604.9	108.7	2	Corresponds to snow samples CEA4-3 # 47, 48, 49	M18 Smoke Grenade
18	4-1	50	496.6	60.0	3	Corresponds to snow samples CEA4-3 # 47, 48, 49	M18 Smoke Grenade

Table E-1 (cont). Metal results (mg/kg) for surface soil samples.

Sample ID	Ag	Al	As	Ba	Be	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	Sb	Se	Tl	V	Zn
1	ND	11,100	2.99	36.9	0.290	2,210	ND	5.53	94.8	6.03	19,400	1,200	2,600	210	137	8.67	18.1	1.51	ND	ND	21.6	32.7
2	ND	10,700	2.88	36.6	0.290	2,450	ND	5.86	85.7	6.83	19,400	1,320	2,770	217	135	9.67	17.7	1.52	ND	ND	20.9	34.7
3	ND	11,100	2.99	39.4	0.300	2,410	ND	5.74	55.1	6.49	19,400	1,330	2,740	210	135	8.96	18.4	1.21	ND	ND	22.0	35.5
4	ND	9,020	1.86	39.6	0.290	4,850	ND	8.48	339	11.4	22,300	1,760	3,740	342	162	14.6	18.4	4.18	ND	ND	20.2	38.3
5	ND	8,930	1.60	40.0	0.293	4,550	ND	8.39	381	11.0	22,500	1,750	3,620	334	169	15.4	18.3	4.63	ND	ND	20.6	37.2
6	ND	9,210	1.43	42.0	0.295	4,840	ND	8.65	413	11.5	22,800	1,880	3,670	369	189	16.4	18.9	4.97	ND	ND	21.2	38.9
7	ND	9,900	2.06	44.6	0.320	3,690	ND	7.90	335	12.3	19,600	1,700	2,960	297	248	13.2	29.9	4.21	ND	ND	21.0	39.4
8	ND	10,000	2.53	44.4	0.320	3,780	ND	8.03	339	14.8	19,800	1,680	2,940	302	241	13.5	23.2	4.22	ND	ND	21.5	44.1
9	ND	10,100	2.19	46.1	0.330	3,720	ND	8.03	346	13.0	19,900	1,720	3,000	306	236	13.8	26.2	4.34	ND	ND	21.5	40.9
10	ND	8,980	1.77	42.7	0.283	3,650	ND	6.85	243	10.6	17,700	1,460	2,680	259	220	10.5	54.8	3.57	ND	ND	19.5	41.1
11	ND	8,720	1.79	42.7	0.275	3,520	ND	6.77	251	32.1	18,000	1,340	2,730	270	174	11.0	24.8	3.36	ND	ND	18.6	42.9
12	ND	9,220	1.63	46.1	0.290	3,720	ND	7.14	294	12.1	18,900	1,480	2,850	285	206	11.8	32.0	3.73	ND	ND	19.4	41.8
13	ND	11,200	2.09	47.4	0.320	3,160	ND	7.49	319	10.6	21,300	1,530	2,900	313	177	12.1	36.8	4.17	ND	ND	23.1	41.5
14	ND	11,300	1.56	48.6	0.325	3,310	ND	7.90	402	10.8	21,200	1,620	2,880	305	200	13.3	38.0	4.97	ND	ND	23.6	41.9
15	ND	11,400	1.99	47.6	0.323	3,280	ND	8.01	384	26.1	21,400	1,600	2,860	300	194	14.0	38.3	4.85	ND	ND	23.8	42.9
16	ND	8,930	1.52	43.6	0.295	2,990	ND	8.43	289	11.7	21,800	1,870	3,070	256	192	13.7	19.9	3.66	ND	ND	21.8	34.0
17	ND	9,730	0.68	46.0	0.320	2,940	ND	9.16	471	12.0	23,400	2,110	3,140	279	256	14.7	39.1	6.14	ND	ND	23.3	34.4
18	ND	7,380	1.16	33.2	0.245	2,520	ND	7.17	254	9.61	19,300	1,570	2,620	220	162	12.0	16.9	3.25	ND	ND	18.5	29.1

Appendix F

The first step is to identify the area where pyrotechnics are utilized and the prevailing wind direction. Next, the type of pyrotechnic devices utilized needs to be noted to determine the size of the decision unit. For example, the degree of dispersion of particulate residues from a smoke grenade will be greater than for a booby trap simulator. The decision unit should be orientated to capture particulate residue in the downgradient prevailing wind direction. In the case of a known area for booby trap detonations it may be possible to sample the entire area of residue with a single decision unit. In other cases, such as deployment of a smoke grenade it may be necessary to have multiple decision units (Figure 29). Decision Units on the order of 10 x 10 m to 100 x 100 m seem appropriate. Each multi-increment sample should consist of 100-increments collected from within the decision unit. The sample should be collected with a plastic scoop to a depth of 2 cm following the same field techniques used for sampling energetic residues (Walsh *et al.* 2005). Sample processing may be different than what is specified in the current USEPA Method 5030B, however research is ongoing in this area and a preferred methodology has not been developed. CRREL's recommendation is that the soil be brought back the laboratory and spread out onto a tray for air drying. Next, the soil should be sieved and separated into > 2 and < 2 mm fractions. Machining of the soil sample may be necessary in some situations but research on this topic is ongoing. If the sample is not ground, the digestate aliquot should be built by collecting 20 increments from the original sample. The remainder of the digestion procedures outlined in USEPA Method 5030B should be followed. It should be noted that USEPA Method 5030B yields poor recoveries for antimony. If antimony is a COPC it may be necessary to modify the digestion acid to increase recovery. Research on the appropriate acid mixture is continuing (Sarbach and Jakob 2011). If antimony or tungsten (Clausen *et al.* 2009a, 2007) are a COPC it may be necessary to modify the digestion acid to increase recovery. Research on the appropriate acid mixture for antimony and tungsten is continuing.

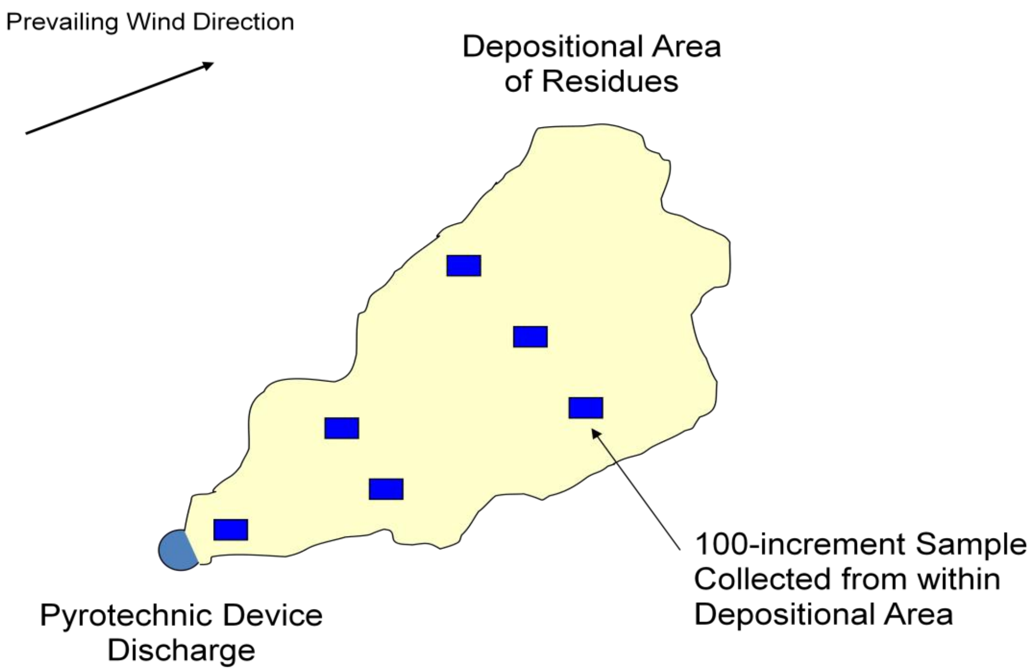

Figure F-1. Proposed sampling approach for a MMRP site where smoke grenades were deployed.